CHEMICAL REVIEWS

VOLUME 31

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RECENT DEVELOPMENTS IN THE CHEMISTRY OF THE BORON HYDRIDES

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I. INTRODUCTION AND DISCUSSION OF NOMENCLATURE

The hydrides of boron have long been of interest because of their unusual chemical properties, and because of their bearing on the problem of valence and of the nature of the chemical bond. According to older valence concepts, current before the introduction of the electron theory, a trivalent element such as boron should form hydrides conforming to the generic formula B_nH_{n+2}. But the simplest such compound, BH_3, although it may have transitory existence as an intermediate in certain reactions, cannot be isolated; it is known only as a dimer, B_2H_6, and in complex compounds in which it is associated with other molecules, such as those of trimethylamine or dimethyl ether. The higher hydrides also fail to conform to the formula B_nH_{n+2}; those the molecular weights

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of which have been determined have the formulas B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$.

The development of the electron theory of valence did not immediately aid in clarifying the difficulty. In the case of diborane, B_2H_6, for example, it is evident that there are only twelve valence electrons; for an ethane-like structure with the usual electron-pair bonds, fourteen valence electrons are required. The same sort of electron deficiency is to be recognized in the higher hydrides.

The problem thus briefly outlined gave rise to numerous suggestions. Some writers took the view that positively charged boron atoms are associated with negatively charged hydride ions; others assumed both trivalent positive and pentavalent negative boron and both positive and negative hydrogen to be present in the structures of these compounds. These earlier hypotheses usually had no experimental basis other than the molecular formulas of the hydrides. On this account, most of them are not discussed in this review; a full set of references has been compiled by Wiberg (62).

Four of these earlier suggestions have, however, received so much attention as to require special mention. One of these, put forward by Wiberg (62), describes diborane as a weak dibasic acid, in which the two boron atoms are joined by a double bond, thus:

$$(H^+)_2 \begin{pmatrix} H & H \\ H\!:\!\ddot{B}\!:\!:\!\ddot{B}\!:\!H \end{pmatrix}^- \quad \text{or} \quad \begin{matrix} H & H \\ \ddot{B} & H^+ & \ddot{B} \\ H\!:\!B & :\ :\ & B\!:\!H \\ & H^+ & \end{matrix}$$
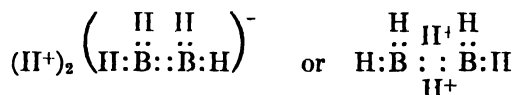
(the second formula is intended to convey the idea that the two hydrogen ions are not entirely free). Numerous arguments for this formulation have been advanced, but there are no experimental facts pointing uniquely in that direction. The behavior of diborane toward ammonia once seemed to yield favorable evidence, but later studies contradicted the earlier interpretation (see pages 23). The parachor is cited by Wiberg as evidence favoring this formulation, but this interpretation also has been criticized by later workers (16).

Another formulation, proposed in slightly different forms by Boeseken, by Wahl, and by Henstock (62), pictures diborane as a monobasic acid, in which one boron atom is coördinatively saturated and the other unsaturated, as shown by the formula

$$H^+ \begin{pmatrix} H & H \\ H\!:\!\ddot{B}\!:\!\ddot{B}\!:\!H \\ \ddot{H} & \end{pmatrix}$$
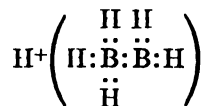
This idea once seemed useful for the interpretation of the reaction of diborane with ammonia, but here, also, facts obtained later are more favorable toward a different interpretation.

A third important suggestion, tending more definitely to accept as real the apparent electron deficiency already mentioned, was made by Sidgwick, who considered it necessary to assume that two of the hydrogen atoms in diborane are attached by single electrons, instead of doublets (33). With the develop-

ment of the concept of resonance, this suggestion was generalized to include all of the structures represented by the formulas

$$\text{H:}\overset{\text{H}}{\underset{\text{H}}{\ddot{\text{B}}}}\text{:}\overset{\text{H}}{\underset{\text{H}}{\ddot{\text{B}}}}\text{:H}, \quad \text{H}\cdot\overset{\text{H}}{\underset{\text{H}}{\ddot{\text{B}}}}\text{:}\overset{\text{H}}{\underset{\text{H}}{\ddot{\text{B}}}}\text{:H}, \quad \text{and} \quad \text{H:}\overset{\text{H}}{\underset{\text{H}}{\ddot{\text{B}}}}\cdot\overset{\text{H}}{\underset{\text{H}}{\ddot{\text{B}}}}\text{:H}$$
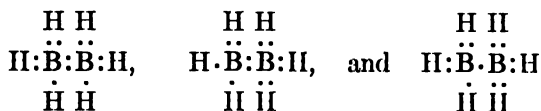
to which more recently were added (19) structures such as

$$\text{H}^{+}\overset{\text{H}}{\underset{\text{H}}{\ddot{\text{B}}}}\text{:}\overset{\text{H}}{\underset{\text{H}}{\ddot{\text{B}}}}^{-}\text{:H} \quad \text{and} \quad \text{H:}\overset{\text{H}}{\underset{\text{H}}{\ddot{\text{B}}}} \ \overset{\text{H}}{\underset{\text{H}}{\ddot{\text{B}}}}\text{:H}$$
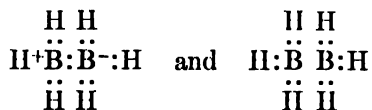
Similar types of resonance are to be considered also for the other boron hydrides.

In the formulas so far discussed, the boron atoms are regarded as directly linked to each other. According to the fourth general viewpoint requiring discussion here, these atoms are indirectly linked, through hydrogen atoms forming a bridge, as represented by the following formula:

This suggestion, originally made by Dilthey and later somewhat modified by Core (62), has been reviewed and extended by Nekrasov (18), who has, however, not advanced decisive evidence in its favor. It is to be recognized that this formulation easily accounts for many of the chemical properties of diborane; it also accounts for the diamagnetism of this substance, and, as pointed out rece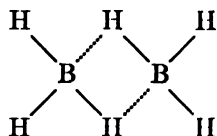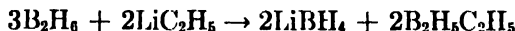ntly by Stitt, it offers one interpretation of the relatively high potential barrier to internal rotation which is indicated by specific-heat measurements (35). The results derived from the Raman spectrum (1) also seem compatible with this picture. Nevertheless, the picture drawn here is not in agreement with the results of electron-diffraction studies (2).

All of the ideas here discussed, as well as some not specifically mentioned, have had value in the development of the subject and are supported by some observations. Nevertheless, it must be recognized that no single picture of diborane is in satisfactory agreement with either the total chemical behavior of the substance or deductions from the various physical properties so far studied.

Numerous structures have been proposed for the higher boron hydrides, but knowledge of their chemical properties is still too meagre to give support to any of these suggestions. Since Bauer in the following review (2) discusses in detail the physical data bearing upon the structure of diborane and of the higher hydrides, structural problems will not be further discussed in this review, except as they are directly related to the chemical aspects of the subject.

Quite aside from these structural problems, the chemistry of the boron hydrides is so unusual as to be a matter of considerable interest in itself. The

unique behavior of these substances may be briefly indicated by listing some of the better-known reactions of diborane, the simplest and most thoroughly studied member of the group:

$$5B_2H_6 \rightarrow 2B_5H_{11} + 4H_2$$

$$2B_5H_{11} + 2H_2 \rightarrow 2B_4H_{10} + B_2H_6$$

$$B_2H_6 + 2Na \rightarrow Na_2B_2H_6$$

$$B_2H_6 + HCl \rightarrow B_2H_5Cl + H_2$$

$$5B_2H_6 + 2B(CH_3)_3 \rightarrow 6B_2H_5CH_3$$

$$B_2H_6 + 2CO \rightarrow 2BH_3CO$$

$$B_2H_6 + 2N(CH_3)_3 \rightarrow 2BH_3N(CH_3)_3$$

$$B_2H_6 + 2NH_3 \rightarrow B_2H_6 \cdot 2NH_3$$

$$B_2H_6 + 4CH_3OH \rightarrow 2BH(OCH_3)_2 + 4H_2$$

$$B_2H_6 + 4CH_3CHO \rightarrow 2BH(OCH_2CH_3)_2$$

$$6B_2H_6 + Al_2(CH_3)_6 \rightarrow 2AlB_3H_{12} + 3B_2H_4(CH_3)_2$$

$$3B_2H_6 + 2LiC_2H_5 \rightarrow 2LiBH_4 + 2B_2H_5C_2H_5$$
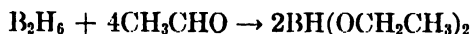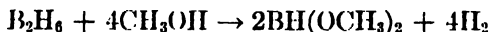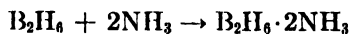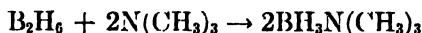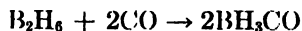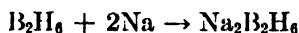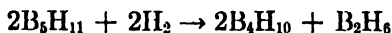
The preceding equations are not always to be taken as complete representations of the reactions; for example, the equilibria involving diborane and hydrogen include hydrides other than the tetraborane and pentaborane shown in the equations. Similarly, the reaction between diborane and trimethylboron yields not only monomethyldiborane, but three higher methyl derivatives as well. The same is true of other reactions in which specific alkyl derivatives of diborane are shown as reaction products. Indeed, one of the striking characteristics of the boron hydrides and their derivatives is their extreme lability: thus, nearly all of the other boron hydrides can be obtained from diborane by reactions proceeding under mild conditions of temperature and pressure; furthermore, the methyldiboranes readily disproportionate into each other, yielding also diborane or trimethylboron.

Such reactions are reminiscent of the cracking and alkylation of hydrocarbons. In the case of the boron hydrides, however, reactions of this type usually proceed at low temperatures and without catalysts. It is possible, therefore, that a study of the mechanisms of these reactions will throw light upon the analogous reactions of carbon chemistry. There are other directions in which the future study of the boron hydrides may prove valuable in leading to a better understanding of the mechanisms of reactions in which boron itself is not involved. Thus, an investigation of the interaction of diborane with aldehydes, ketones, and esters has thrown light on the mechanism by which other reactions of these organic substances may proceed. Another possibility is found in the striking parallelism between the chemical and physical properties of borine carbonyl,

BH$_3$CO, and those of the carbonyls of the transition elements–a parallelism which suggests that a full understanding of the structure of borine carbonyl may prove to be of importance in elucidating the more complex metal carbonyls. Finally, we call attention to the most recent development in the field of borane chemistry, the discovery of the metallo borohydrides. Some of these are highly volatile and therefore of particular interest to those engaged in the study of metallic elements. These and other matters of general interest justify a review of the hydrides of boron at the present time, although there are still many unexplored aspects of their behavior, and hypotheses concerning their structures are likely still to undergo considerable modification.

Before the detailed discussion of the subject under review is undertaken, it should be pointed out that no thoroughly uniform and consistent nomenclature has been adopted for the hydrides themselves, or for several new types of compounds discovered in the course of investigations of the hydrides. Although the name "diborane" is in general use for the compound B$_2$H$_6$, divergence in nomenclature occurs in the case of the higher hydrides. Thus it has been proposed to designate as boranes those hydrides to which the generic formula B$_n$H$_{n+4}$ is applicable and to designate as dihydroboranes those (B$_4$H$_{10}$ and B$_5$H$_{11}$) which may be represented by the formula B$_n$H$_{n+6}$. Since there is only one instance in which the latter term has any advantage of convenience, and since it corresponds to no established structural characteristic, we shall use in this review only names derived from "borane" for the hydrides containing more than one boron atom. The hypothetical molecule BH$_3$ is called borine.

For substances formally to be considered as substitution products of the boranes, a nomenclature derived from the practise in organic chemistry is followed: e.g., B$_2$H$_5$Cl is called chlorodiborane, and the symmetrical dimethyl derivative, B$_2$H$_4$(CH$_3$)$_2$, is named 1,2-dimethyldiborane. The term "borane salts" is employed for compounds formed by addition of metals to the boranes, whereas other salts containing the same constituents, but in different proportions, are designated as metallo borohydrides, for reasons discussed later in the review.

The most difficult problems of nomenclature arise in connection with substances considered to be "addition compounds" of borine and of its derivatives. According to the point of view adopted in this review, these compounds are the result of the union of a borine type of molecule, which lacks an electron pair, with a molecule containing an unshared electron pair. In other words, the "addition compounds" are the products of an acid–base reaction in the sense in which G. N. Lewis uses this term. In products of this type, the basic constituent is usually named first; consequently, we shall use such terminology as trimethylamine-borine and dimethyl ether-borine for the compounds originally named borine trimethylammine and borine etherate, respectively. Their composition will be represented by formulas such as (CH$_3$)$_3$N:BH$_3$ and (CH$_3$)$_2$O:BH$_3$. The use of a single dot will be limited to cases in which there is considerable doubt about the structure.

In a number of instances no names have been as yet assigned to compounds

the structures of which are unknown or not finally determined with respect to all details. In other instances, we have accepted the names used in the original publications. For example, the substance BH_3CO is designated borine carbonyl, in order to call attention to its similarity to other carbonyls. On the other hand, the rather convenient term "diammoniate of diborane" has been retained, even though the interpretation of its structure, favored in this review, is that it is a monoammonium salt, $NH_4(H_3BNH_2BH_3)$. To indicate its unsystematic character, we enclose the term "diammoniate" in quotation marks, whenever it is used in this and similar connections. One or two other questions of nomenclature are taken up in the body of the review.

II. OLDER KNOWLEDGE OF THE BORANES

The existence of compounds of boron with hydrogen has been recognized for a long time, but the compounds are so unstable and so reactive toward air and

TABLE 1

Physical constants of the boranes

NAME	MOLECULAR FORMULA	DENSITY	MELTING POINT	BOILING POINT	VAPOR TENSION	REFERENCE
			°C.	°C.	mm.	
Diborane.............	B_2H_6	0.577 (−183°C.) 0.447 (−112°C.)	−165.5	−92.5	225 (−111.9°C.)	(36)
Tetraborane.........	B_4H_{10}	0.56 (−35°C.)	−120	18	388 (0°C.)	(36)
Stable pentaborane..	B_5H_9	0.61 (0°C.)	−46.6	48	66 (0°C.)	(36, 54)
Unstable pentaborane	B_5H_{11}		−123	63	53 (0°C.)	(8)
Hexaborane.........	B_6H_{10}	0.69 (0°C.)	−65		7.2 (0°C.)	(36)
Decaborane.........	$B_{10}H_{14}$	0.92 (99°C.) 0.78 (100°C.)	99.7	213	19 (100°C.)	(36)

moisture that very little progress was made in their investigation until Stock developed a special technique (36, 37) for dealing with substances possessing such properties. This technique, the early history of the compounds, and the knowledge gained about them up to the year 1932, have been reviewed by Stock in his Baker Lectures at Cornell University (36). Since that time there has been considerable development in this field, made possible largely by more efficient and convenient methods of preparation of the boranes than were available for Stock's earlier work. It therefore seems most appropriate to treat very briefly the work already so carefully reviewed by Stock, and to devote the major portion of this review to a survey of the developments since the appearance of Stock's book. Because of the close relationship between the subjects studied during the two periods, it will not always be possible to treat them quite independently.

The first boron hydride which was definitely characterized as a chemical individual was tetraborane (B_4H_{10}), which Stock and Massenez (46) obtained by

the action of hydrochloric acid upon magnesium boride. Even at the outset, it was recognized that small proportions of heavier boranes were present in the volatile reaction products, but the total yields were very small (less than 3 per cent of the boron) and the presence of silicon hydrides (formed in some 30 per cent yield from the silicide impurity in the boride) made the process of purification very difficult. As a result, several years elapsed before a very stable pentaborane (B_5H_9), a less stable hexaborane (B_6H_{10}), and a trace of the especially stable decaborane ($B_{10}H_{14}$) could be definitely proved to be present in the less volatile fractions (39, 42). The difficulty of handling these substances was due chiefly to their instability and activity toward air, moisture, and the available stopcock lubricants. Stock therefore found it necessary to develop the special technique already mentioned; it involves high-vacuum low-temperature distillations, and the complete exclusion of all substances other than glass and mercury (36, 37).

Studies on the thermal decomposition of tetraborane soon led to the discovery of diborane (38) and this in turn, on long standing, gave very small yields of an unstable pentaborane having the formula B_5H_{11} (54). The latter completes the list of definitely known pure hydroborons; these are characterized physically in table 1. Other boron hydrides are capable of existence; most of these, however, are difficult to handle in the vacuum apparatus (either because they are non-volatile or because they are extremely unstable), and hence have not been recognized as chemical individuals.

A. Thermal stabilities

The least stable of the six compounds listed in table 1 is the pentaborane B_5H_{11}, which may show signs of irreversible decomposition within an hour at room temperature. When heated or allowed to stand for long periods of time, it produces diborane, tetraborane, hydrogen, the stable pentaborane, a faint trace of decaborane, and brown non-volatile liquids and solids (8). Tetraborane is slightly more stable; its decomposition leads to similar products. Both of these compounds probably are involved in the formation of numerous volatile and non-volatile materials from diborane, but it is not possible at present to assign to either a definite rôle in the process. In particular, the belief that the unstable pentaborane is a direct intermediate in the formation of decaborane appears to be unfounded (8, 54).

Diborane, the most thoroughly studied of the boron hydrides, is sufficiently stable to be stored in sealed bulbs (preferably containing some hydrogen) with losses not necessarily exceeding 10 per cent during a year. At 100°C., it rather rapidly produces non-volatile white and brown products, traces of tetraborane and the unstable pentaborane, and ultimately some of the stable pentaborane and decaborane. The formation of the last two is favored by an increase of temperature up to 150°C. A non-volatile brown solid, formulated as $(BH)_x$, has been obtained from diborane in a silent electric discharge (48).

At ordinary temperatures, hexaborane slowly undergoes complete decomposition, yielding hydrogen, a trace of diborane, and a non-volatile solid substance

the hydrogen content and molecular weight (determined cryoscopically in benzene) of which suggest the molecular formula $B_{26}H_{36}$ (42). This complete decomposition of hexaborane at room temperature indicates that it is less stable than diborane; nevertheless it is not completely destroyed when passed at low pressure through a tube at 300°C. (42).

The most stable of the volatile boranes are the pentaborane B_5H_9 and decaborane. The former decomposes only very slowly at 150°C. During some years at room temperature, it produces a small quantity of non-volatile material and hydrogen. Decaborane is quite permanent at room temperature, and can be heated for considerable periods of time at 150°C. without observable change; its decomposition becomes noticeable at 170°C.

B. Chemical reactions of the boranes with other substances

(1) *Oxygen:* Some of the boron hydrides are very sensitive to atmospheric oxygen, while others are but little affected. Both of the pentaboranes are spontaneously inflammable in air at ordinary temperatures. Decaborane explodes in oxygen only at elevated temperatures (e.g., 100°C.), while hexaborane at room temperature reacts with air only slowly. Diborane and tetraborane seem to have flash points slightly above room temperature (36); the former may remain in intimate mixture with air for 3 to 5 days, after which the mixture explodes with great violence (24). The products of these reactions are brown or black solids of indefinite composition.

(2) *Water:* The rates of hydrolysis of the boron hydrides vary over a wide range. Diborane reacts almost instantaneously, according to the equation (41):

$$B_2H_6 + 6HOH \rightarrow 6H_2 + 2B(OH)_3$$
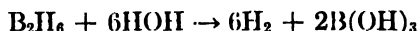
Tetraborane and the unstable pentaborane also are readily hydrolyzed, especially at slightly elevated temperatures or in acid solutions, to yield boric acid and hydrogen. It is the slightly slower rate of hydrolysis which makes possible the preparation of tetraborane by the reaction of magnesium boride with an aqueous solution of an acid,—a solution in which diborane is instantly destroyed. The hydrolysis of the stable pentaborane, of hexaborane, or of decaborane can be completed only by long heating, preferably in acid solution. In all cases, however, the hydrolysis reaction is a feasible first step in an elementary analysis of the volatile boranes or their derivatives.

Neither for the hydrolysis of magnesium boride nor for the reactions of the boranes with water has any mechanism been established. Nevertheless, certain published suggestions require discussion. To explain the former reaction, it has been assumed (62) that the boride contains a group of four boron atoms, as indicated by the formula $(B_4)Mg_6$. The first step in the reaction is supposed to be the formation of the compound $(B_4H_6)(MgOH)_6$, which then is believed to hydrolyze in two ways, yielding $[B_4(OH)_6](MgOH)_6$ in one reaction, and small proportions of tetraborane, hydrogen, and magnesium hydroxide in the other. In support of these assumptions, it is claimed that the salt $[B_4(OH)_6](NH_4)_6$ has been isolated, but the formula is based only upon analyses and a molecular weight

calculated from the freezing-point depression, without regard for activity coefficients which might have been important.

For the reaction of diborane with water, ten steps are postulated (62). Of the nine compounds assumed to be formed as intermediates, five are admittedly unknown; three are hypothetical and but vaguely related to the products of the hydrolysis of magnesium boride (62, references to the work of Ray and of Travers, Ray, and Gupta), and only one, formulated as $H_2[H_2B(OH)B(OH)H_2]$, can be directly related to diborane. Even this is known only as a potassium salt, and its structure remains largely hypothetical. This salt, formed by the action of diborane upon solutions of potassium hydroxide, is discussed more fully on page 33.

A simpler interpretation of the reaction between diborane and water involves the assumption that a borine derivative, $H_2O:BH_3$, is formed as an intermediate step (18). Although the behavior of diborane toward trimethylamine and toward dimethyl ether (see pages 16 and 19) lends support to such a possibility, it seems premature, on the basis of the meagre data as yet available, to attempt a critical evaluation of this or other ideas on the subject.

(3) *Ammonia:* The reactions of the boron hydrides with ammonia have led to the discovery of a number of unusually interesting types of compounds, the study of which has had considerable bearing on the development of hypotheses concerning the structural principle of the hydrides. Although most of the compounds involved were discovered in the period summarized in this section of the review, many important developments occurred later. For the present, therefore, we shall review briefly these compounds, most of which have been already described in detail in Stock's book (36), and shall leave critical discussion to a later section (page 22).

At $-120°C.$, *diborane* reacts quantitatively with two volumes of ammonia, yielding a salt-like product which is quite stable at room temperature (42, 50). *In vacuo* it melts at 90°C. and gives off hydrogen. The compound is commonly called the "diammoniate of diborane," although it is more properly to be formulated as some type of ammonium salt. This "diammoniate" reacts with additional ammonia at $-50°C.$ The significance of this fact will be discussed later.

The ammoniates of the higher hydrides are not well understood. *Tetraborane* forms a "tetrammoniate" (53) which seems to be a diammonium salt, capable of undergoing a complicated secondary reaction with ammonia. At $-40°C.$ *in vacuo* it is transformed by loss of ammonia into a product approximately described by the formula $B_4H_{10}\cdot2NH_3$; at higher temperatures, hydrogen also is evolved (24). The *stable pentaborane* forms a "diammoniate," $B_5H_9\cdot2NH_3$, in which only one of the nitrogen atoms seems to be present as ammonium ion (24). A further, slow reaction with ammonia leads to the formation of a "tetrammoniate" (53), two of the nitrogen atoms of which seem to function as ammonium ions (24). A product having the same composition as this "tetrammoniate" is formed by the reaction of ammonia with the *unstable pentaborane* (50). It is not certain, however, that any of the ammoniates of the pentaboranes are single substances, rather than mixtures of degradation products. The behavior of

hexaborane toward ammonia has not been studied. *Decaborane* forms a "hex-ammoniate" which, unlike the compounds obtained from the other hydrides, is readily decomposed into the parent substances (53).

The reactions just described occur at low temperatures; at elevated temperatures, a wider variety of products may appear. Thus diborane reacts with ammonia, present in excess, to yield boron imide, $B_2(NH)_3$, which decomposes, on further heating, to form boron nitride (51). When the proportions of diborane and ammonia are those of the "diammoniate," or when this substance itself is heated, the volatile compound $B_3N_3H_6$ is obtained in yields as high as 45 per cent. A study of the conditions favoring high yields of this compound has appeared recently; for details the original article (63) should be consulted. The same compound is formed also by the action of ammonia on tetraborane or on either of the pentaboranes (36), but not from decaborane (53).

The benzene-like structure of the stable compound $B_3N_3H_6$ was recognized by Stock and Pohland (51), and was confirmed by electron-diffraction studies (2, 61) as well as by the preparation of methyl derivatives (page 29). Because of its structural similarity to benzene, the name borazole was suggested by H. Wieland (63); in spite of its unsystematic character, this designation has the advantage of brevity, and we shall use the name borazole rather than the more formal name, triborine triamine, in this review.

Another product of the reaction of diborane with ammonia is the compound B_2H_7N; both this substance and borazole will receive more detailed discussion later (pages 25 and 27).

(4) Halogens: Three of the volatile boranes are known to react vigorously with halogens, and the others undoubtedly would behave similarly if the appropriate experiments were tried. *Diborane* may be converted to chlorodiborane or bromodiborane by reaction with chlorine or bromine, smoothly only at very low temperatures (43). The action of iodine yields products difficult to isolate, but iododiborane can be prepared by the (uncatalyzed) reaction of hydrogen iodide with diborane (52):

$$B_2H_6 + HI \rightarrow B_2H_5I + H_2$$
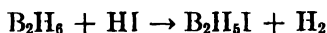
This iodo derivative is of interest because it may be converted partially to tetraborane by treatment with sodium amalgam (52):

$$2B_2H_5I + 2Na \rightarrow B_4H_{10} + 2NaI$$
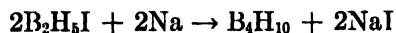
Hydrogen bromide attacks diborane in the manner of hydrogen iodide, but the corresponding reaction with hydrogen chloride usually requires the presence of a catalyst such as aluminum chloride (36) or boron chloride (24). Far more efficient for the preparation of chloro- and bromo-diboranes are the reactions of the corresponding boron halides with diborane, as illustrated by the following equation (22):

$$5B_2H_6 + 2BCl_3 \leftrightarrows 6B_2H_5Cl$$

The isolation of chlorodiborane by this method (6) is made difficult by the rapidity and extent of the reverse reaction in the absence of excess boron chloride; conditions are more favorable in the case of bromodiborane.

The reaction of *tetraborane* with hydrogen chloride proceeds very slowly even in the presence of aluminum chloride. Heating does not help, because tetraborane is too unstable. No chloro derivatives of tetraborane have been isolated; instead, only chlorinated degradation products are obtained (58).

Decaborane and the stable *pentaborane* are unaffected by either hydrogen chloride or boron chloride, but they submit to direct attack by halogens. The reaction

$$B_5H_9 + Cl_2 \rightarrow B_5H_8Cl + HCl$$
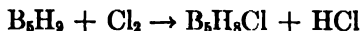
can be controlled at $-80°C$.; the chief product, which has the composition of a monochloro derivative, probably is a mixture of isomers differing little in volatility, but more in stability (24). The halogenation of decaborane occurs slowly at room temperature and leads to a variety of products, among which are substances formulated as $B_{10}H_{12}Br_2$ and $B_{10}H_{12}I_2$ (43, 53).

(5) *Metals:* Diborane reacts with sodium amalgam to produce the interesting salt-like compound $Na_2B_2H_6$; several other metals react in similar fashion (42). Although these reactions were discovered early in the history of the boron hydrides, most of the information about the compounds thus obtained is of relatively recent origin, and they are accordingly reviewed in a later section (page 33).

III. DEVELOPMENTS IN BORON HYDRIDE CHEMISTRY SINCE 1931

A. *Preparation of the boranes*

Previous to the year 1931, the chief obstacle to the increase in knowledge of the boron hydrides was the great difficulty and expense of preparing the hydrides by the boride–acid method in quantities sufficiently large for thorough study. The preparation of an active magnesium boride is in itself a cumbersome task; the conversion of the boride to the hydrides is a very time-consuming procedure which gives very poor yields. Although this method (as yet the only satisfactory source of hexaborane) has been materially improved by the use of phosphoric acid (34) instead of hydrochloric acid, the total yields do not exceed 11 per cent (64), and the process still is a very slow one, involving troublesome impurities.

The situation was greatly improved by the development of a new method, which consists essentially of the hydrogenation of boron chloride or bromide by the aid of a fairly powerful electric discharge. According to the original description of the procedure (22), pure hydrogen is allowed to bubble through liquid boron chloride at $-40°C$., and the resulting mixture (10 moles of hydrogen per mole of boron chloride) is led through a 12- to 15-kilovolt ($\frac{1}{4}$ K.V.A.) discharge at a pressure of 10 mm. The resulting hydrogen chloride, chlorodiboranes, and unused boron chloride are condensed from the excess hydrogen, and fractionated

to remove the hydrogen chloride (6).   The fractionating column then is operated at a pressure of 2 atm. (reflux temperature, 0°C.), in order to attain a temperature favorable to rapid decomposition of the chlorodiboranes, according to equations such as

$$6B_2H_5Cl \leftrightarrows 5B_2H_6 + 2BCl_3$$

Because of the reversibility of these reactions, it is well to remove the diborane as rapidly as it is formed, and the fractionating column does this very well (24). The fractions rich in hydrides are subjected to a further process of fractional condensation, and the diborane finally is purified by a direct vacuum distillation from a tube at −150°C.

A later improvement in this process substitutes boron bromide for the chloride (55); the advantage is due to the fact that the decomposition of bromodiboranes to diborane

$$6B_2H_5Br \leftrightarrows 5B_2H_6 + 2BBr_3$$

is more easily brought to completion than that of the chloro derivatives, because the volatility of boron bromide is such that it is relatively easy to remove this substance from the reaction mixture; also more favorable is the relative ease with which the diborane may be purified from bromine-containing impurities, rather than from the corresponding chlorine compounds.   The recent development of an easy and efficient method of preparing boron bromide (14) avoids the difficulty which formerly stood in the way of its use.

A large portion of the boron halide passes through the discharge without evident change, and is readily recovered; of that reacting, 60 to 75 per cent can be converted to diborane when boron chloride is the starting material, and up to 80 per cent when the bromide is used.

The new method of preparing diborane also made other boron hydrides more readily available.   Diborane, tetraborane, the unstable pentaborane, and hydrogen constitute a system involving several sets of equilibria which are attained at different rates (8).   Furthermore, this system of equilibria is not entirely stable, for there is also a slow, irreversible production of the stable pentaborane and of decaborane.   Consequently, by suitably controlling the temperature, the time of heating, and the relative proportions of the components, the desired borane may be obtained in yields sufficiently high to warrant its separation from the mixture.   Hexaborane is involved to a slight extent in this system (47), but it is best prepared by Stock's original method (41).   For a very unstable octaborane (8), apparently present as a slight trace among the products of this set of reactions, no satisfactory preparatory method has been developed.

The conditions best suited to the preparation of the four better-known higher hydrides of boron are given in the following paragraphs.   For details, the original references must be consulted.

The unstable pentaborane may be prepared by allowing diborane to flow through a U-tube heated to 115°C.   The rate of flow of diborane (as it evaporates from a tube at −80°C.) is controlled by a capillary tube so as to make the treatment

roughly equivalent to a 2-min. heating of a stationary sample. The product is purified by fractional condensation, and the recovered diborane is put through the process repeatedly until the desired quantity of unstable pentaborane is obtained. In terms of diborane transformed, the yield is nearly 90 per cent, but the fraction of diborane undergoing change in a single passage through the heated tube is small. The product usually is contaminated with about 3 per cent of the stable pentaborane, unless milder heating is employed; tetraborane is a by-product (8).

Tetraborane is obtained by heating a mixture of hydrogen and the unstable pentaborane (molecular ratio about 10:1) for 10 min. at 100°C., in a bulb of such dimensions that the pressure rises to about 1.5 atm. In terms of the pentaborane used up (75 per cent), the yield is approximately 85 per cent, as calculated according to the equation

$$B_5H_{11} + H_2 \rightarrow B_4H_{10} + \tfrac{1}{2}B_2H_6$$
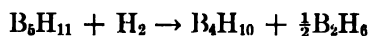
Longer heating lowers the yield because of the transformation of some of the tetraborane into diborane (8).

The simultaneous preparation of tetraborane and the unstable pentaborane from diborane has been carried out by the use of a magnetically operated circulating pump, sending diborane at an initial pressure of 140 mm., first through a furnace at 180°C., and then through a trap at −115°C. (adequate for condensing the products, but allowing diborane to go through). This method offers a certain convenience, but requires a more elaborate apparatus (47).

The stable pentaborane is prepared most efficiently by the use of the circulating-pump apparatus, employing diborane at an initial pressure of 120 mm. It passes through a 10 x 160 mm. tube in which mercury is vaporized at 250°C.; the rate of flow is 50 cc. (S.C.) per minute. Of the diborane used up during a 4-hr. operation, 56 per cent is converted to the stable pentaborane, and 26 per cent to the unstable pentaborane. Small but significant quantities of hexaborane also are obtained. Similar results are achieved in half the time if the temperature of the hot tube is 300°C., but these conditions lead to a lower yield of the unstable pentaborane (47).

A similar flow process could be operated without the special pump, but would then be far less convenient. The heating of diborane in a sealed bulb (best in the presence of a catalyst such as boron chloride) leads to yields of approximately 30 per cent of the diborane used up. This method is less efficient, but is convenient for small quantities of the product (8, 22).

Decaborane is obtained in 30 per cent yields from diborane in a sealed bulb, one side of which is heated to 160°C. (pressure slightly above atmospheric) (24). It is obtained also by heating tetraborane (39), or by the circulating-flow heating of the unstable pentaborane (38 mm., 250°C., and 12 cc. per minute) (47).

B. Preparation and properties of the alkyldiboranes

The discovery that the formation of diborane and boron chloride from chlorodiboranes is a reversible reaction (see page 12) suggested that it might be

possible to prepare alkyl derivatives of diborane by the reaction of trimethyl-boron with diborane. Actually, when a mixture of these two reactants is left for a few hours at room temperature, it becomes possible to isolate four methyl derivatives of diborane (32). The positions of the methyl groups in these compounds have been demonstrated by hydrolytic reactions, according to the following equations:
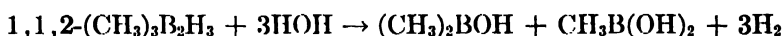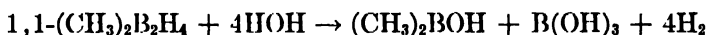
$$CH_3B_2H_5 + 5HOH \rightarrow CH_3B(OH)_2 + B(OH)_3 + 5H_2$$

$$1,1\text{-}(CH_3)_2B_2H_4 + 4HOH \rightarrow (CH_3)_2BOH + B(OH)_3 + 4H_2$$

$$1,1,2\text{-}(CH_3)_3B_2H_3 + 3HOH \rightarrow (CH_3)_2BOH + CH_3B(OH)_2 + 3H_2$$

$$1,1,2,2\text{-}(CH_3)_4B_2H_2 + 2HOH \rightarrow 2(CH_3)_2BOH + 2H_2$$

TABLE 2

Physical constants of the alkyldiboranes

FORMULA	MOLECULAR WEIGHT		MELTING POINT	BOILING POINT	CHARACTERISTIC VAPOR TENSION		REFERENCE
	Observed	Calculated			Pressure	Temperature	
			°C.	°C.	mm.	°C.	
$CH_3B_2H_5$	Normal	41.7			55	−78.5	(32)
$(CH_3)_2BHBH_3$	54.3	55.7	−150.2	−2.6	10	−78.5	(32)
$(CH_3BH_2)_2$	55.6	55.7	−124.9	+4.9	7	−78.5	(25)
$(CH_3)_2BHCH_3BH_2$	68.9	69.7	−122.9	45.5	123	0	(32)
$[(CH_3)_2BH]_2$	83.95	83.75	−72.5	68.6	48	0	(32)
$C_2H_5B_2H_5$	56.1	55.7	Glassy		7	−78.5	(26)
$(C_2H_5)_2BHBH_3$	83.6	83.75	Glassy	67	42	0	(26)
$(C_2H_5)_2BHBH_2C_2H_5$		111.8	Glassy		4	0	(26)
$[(C_2H_5)_2BH]_2$		139.8	Glassy		0.5	0	(26)
$n\text{-}C_3H_7B_2H_5$	71.1	69.7	Glassy		6.2	−60	(26)
$(n\text{-}C_3H_7)_2BHBH_3$		111.8	Glassy		2.8	0	(26)

Although the symmetrical dimethyldiborane, $1,2\text{-}(CH_3)_2B_2H_4$, has not been found among the reaction products of diborane with trimethylboron, it has been prepared by a special method to be described later (page 20). Four analogous ethyl derivatives have been prepared by the reaction of diborane with triethyl-boron. Mono-*n*-propyl- and 1,1-di-*n*-propyl-diboranes also have been obtained by the exchange of the alkyl group for hydrogen (26). The physical constants of all of the known alkyldiboranes are summarized in table 2.

Chemical studies of these alkyl derivatives have led to a number of interesting observations. Like diborane, they react vigorously with air or with moisture, but they are far more stable against decomposition with loss of hydrogen. Thus, a mixture containing chiefly tri- and tetra-methyldiboranes, together with an excess of trimethylboron, has been kept for several years at room temperature, and has been heated to 200°C. without irreversible change (24). On the other hand, disproportionation reactions occur quite readily; because of the

formation of the nearest members of its series, any one of the pure derivatives soon becomes impure if allowed to stand at room temperature. The isolation of the pure derivatives, therefore, is a fairly difficult task, achieved only by low-temperature, low-pressure fractionation; in each case the product remains pure only if the temperature is sufficiently low practically to eliminate the vapor phase.

It has been observed that derivatives in which two alkyl groups and one hydrogen atom are attached to boron are more stable than those having only one alkyl group attached to boron. Thus, symmetrical dimethyldiborane is rapidly converted at room temperature into the unsymmetrical derivative (25), a fact which explains the absence of the former among the products of the reaction of diborane with trimethylboron. Similarly, monomethyldiborane so rapidly produces diborane and dimethyldiborane that it has not been possible to measure its vapor tension with precision; trimethyldiborane, which likewise contains the CH_3BH_2 unit, somewhat more slowly produces 1,1-dimethyldiborane and tetramethyldiborane. Other chemical properties of the alkyl derivatives are described in later sections (pages 16, 19, 25 and 29).

Irrespective of the magnitude of the excess of trialkylboron employed in the preparation, not more than four of the six hydrogen atoms of diborane are replaced by alkyl groups. Furthermore, no derivative of diborane in which three alkyl groups are attached to the same boron atom ever has been obtained. These facts have been used to support two ideas: (1) that two of the six hydrogen atoms in diborane are bound differently from the others, and (2) that the presence of hydrogen is essential to the formation of such a boron-to-boron link as that in diborane. Such conclusions are, however, not necessarily valid, since other explanations (e.g., steric hindrance) are conceivable.

IV. COÖRDINATION COMPOUNDS OF BORINE

Early in his work on the boranes, Stock demonstrated that the molecule of diborane is not thermally dissociated into two borine (BH_3) molecules at temperatures as high as 150°C. (42). Nevertheless, even at relatively low temperatures, diborane reacts with substances, the molecules of which contain unshared electron pairs, to produce coördination compounds of borine. The breaking of the boron–boron bond thus occurs rather readily when it results, not in the formation of two electronically unsaturated borine $\left(\begin{array}{c} H \\ \ddots \\ H:B \\ \ddots \\ H \end{array}\right)$ molecules, but in the production of coördinatively and electronically saturated substances such as trimethylamine-borine:

$$(CH_3)_3N:\overset{\cdot\cdot}{\underset{\cdot\cdot}{B}}:H$$
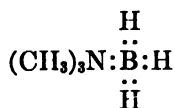
The formation of compounds of this type is of such importance in the chemical behavior of diborane, and probably of the other boranes as well, that most of the

chemical reactions of these substances cannot be adequately discussed without reference to this property. For this reason, considerable space is given to a description of the borine complexes, with special emphasis on those which have a direct bearing on other phases of boron hydride chemistry, or on the question of the possible transitory existence of borine itself.

A. Trimethylamine-borine and related compounds

The reaction of diborane with trimethylamine is rapid and quantitative at temperatures as low as $-110°C.$ (10); the product is trimethylamine-borine, $(CH_3)_3N:BH_3$, a sublimable white solid which is not rapidly attacked by moist air. In the absence of air, it seems to be permanently stable; it may be heated for hours at 125°C. without appreciable decomposition, and has been observed as one of the major products of a nearly quantitative reaction occurring slowly at 200°C. (25). In the presence of hydrochloric acid at 100°C., it is completely hydrolyzed to form boric acid, hydrogen, and trimethylammonium chloride.

TABLE 3

Physical constants of trimethylamine-borine and derivatives

FORMULA	MOLECULAR WEIGHT		MELTING POINT	BOILING POINT	SAMPLE VAPOR TENSION	REFERENCE
	Observed	Calculated				
			°C.	°C.	mm.	
$(CH_3)_3N:BH_3$	74.4	72.9	94	171	0.8 (23°C.)	(10)
$(CH_3)_3N:BH_2CH_3$	88.5	86.9	0.8	177	2.3 (22°C.)	(25)
$(CH_3)_3N:BH(CH_3)_2$	102.2	101.0	-18	172	2.9 (21°C.)	(25)
$(CH_3)_3N:B(CH_3)_3$	Dissociates		120		2.1 (23°C.)	(25)

The action of dry hydrogen chloride causes the stepwise replacement of hydrogen atoms in the BH_3 part of the molecule by chlorine atoms; the first step of the reaction is completed in half an hour at $-80°C.$ (25). The second step of this reaction occurs far more slowly at $+100°C.$ (25), and the third with still more difficulty at 200°C. (24). The resulting chloro derivatives all are difficultly volatile, white solids which have not been investigated in detail.

Trimethylamine-borine can be obtained, not only from diborane, but also by the reaction of some of the higher boranes with trimethylamine (24). The stable pentaborane reacts with trimethylamine to give first the compound $B_5H_9 \cdot 2N(CH_3)_3$, which when heated gives trimethylamine-borine and other products not yet adequately characterized. Tetraborane and the unstable pentaborane react with trimethylamine to yield somewhat impure samples of trimethylamine-borine and a non-volatile solid residue. These reactions deserve further, more detailed study, since they may be helpful in elucidating the structure of the higher hydrides.

Methyl derivatives of trimethylamine-borine have been prepared by the action of trimethylamine upon methyldiboranes and upon trimethylboron (25).

From symmetrical dimethyldiborane the compound $((CH_3)_3N:BH_2CH_3$ has been obtained; tetramethyldiborane produces the compound $((CH_3)_2N:BH((CH_3)_2;$ trimethylboron yields $(CH_3)_3N:B((CH_3)_3$. Monomethyl- and trimethyl-diboranes give mixtures apparently composed of the first two of these derivatives, which are difficult to separate from each other. The physical constants of the complex compounds mentioned here are given in table 3.

The least stable of the four compounds listed in table 3 is the last: the vapor of trimethylamine-trimethylboron is 70 per cent dissociated at 80°C. and 70 mm. pressure. The dimethylborine derivative is stable up to 70°C.; at this temperature it begins to disproportionate slowly, according to the equation

$$2(CH_3)_3N:BH(CH_3)_2 \rightarrow (CH_3)_3N:BH_2CH_3 + (CH_3)_3N + B((CH_3)_3$$

Trimethylamine-monomethylborine, although quite stable at 100°C., disproportionates at 200°C. according to the equation

$$3(CH_3)_3N:BH_2CH_3 \rightarrow (CH_3)_3N:BH_3 + (CH_3)_3N + B((CH_3)_3$$

The monomethyl and dimethyl derivatives react with dry hydrogen chloride as does trimethylamine-borine itself. At -80°C. these reactions are faster than the attack upon the parent substance; the rate increases with the number of methyl groups attached to boron (25).

B. Action of methylamine and of dimethylamine upon diborane

Two moles of methylamine add to 1 mole of diborane to form a compound (28). Unlike the salt-like "diammoniate" of diborane (see pages 9 and 22), this product is liquid at room temperature. It is not volatile at room temperature, nor can it be vaporized by heating, since even a mild increase of temperature causes it to lose hydrogen and to be converted, in good yields, into tri-N-methylborazole (see page 29). No other reactions of the compound are known.

Dimethylamine reacts with diborane to produce a compound, $H_2BN((CH_3)_2$, the formation of which may be preceded by an intermediate addition compound, $(CH_3)_3HN:BH_3$. The end product, $H_2BN(CH_3)_2$, has been called "inorganic isobutylene" by its discoverers, who have not yet published details concerning its preparation or properties (63). The same authors mention also the formation of the compound $[(CH_3)_2N]_2BH$. Both compounds are stable volatile substances having no tendency to disproportionate.

C. Borine carbonyl

Borine carbonyl (10), H_3BCO, is conveniently prepared by heating diborane with a large excess of carbon monoxide in a bomb tube at 100°C. For best results, the pressure should be high (e.g., 20 atm.), as might be expected from the equation

$$2CO + B_2H_6 \rightleftharpoons 2H_3BCO$$

The equilibrium is established within 20 min. and is then fixed by rapid cooling. The three main components of the mixture,—borine carbonyl, diborane, and carbon monoxide,—can be isolated by a process of fractional condensation.

From the quantities found in each of a number of experiments at different pressures, the approximate average value 2.8×10^4 has been calculated for the equilibrium constant,

$$\frac{P_{CO}^2 \times P_{B_2H_6}}{P_{H_3BCO}^2}$$

at 100°C. (partial pressures expressed in millimeters of mercury).

Borine carbonyl melts at −137.0°C. and boils at −64°C. (as extrapolated from the equation $\log_{10} p_{mm.} = 7.850 - 1040/T$).

At room temperature, borine carbonyl decomposes into diborane and carbon monoxide at a very rapid rate which is, however, very sharply decreased long before equilibrium is established. The inhibiting factor evidently is the carbon monoxide developed by the reaction, for a mixture of diborane with the carbonyl (either put together directly, or remaining after the removal of carbon monoxide) shows the rapid, but soon diminishing, rise of pressure characteristic of a fresh sample of the carbonyl. Particularly significant is the fact that the admixture of an equal volume of carbon monoxide to the pure borine carbonyl almost entirely prevents the decomposition.

These observations are easily explained on the assumption that the first stage of the decomposition is the rapid and highly reversible reaction

$$H_3BCO \rightleftarrows CO + BH_3$$
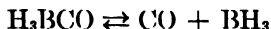
The second stage is assumed to be the nearly irreversible reaction

$$2BH_3 \rightarrow B_2H_6$$
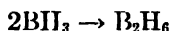
A high concentration of carbon monoxide would, according to the first assumption, greatly decrease the concentration of borine (BH_3), and this would mean that the rate of the second stage would be greatly diminished, especially as this stage appears to be a second-order reaction with respect to borine.

Although this relatively simple explanation of the inhibiting effect of carbon monoxide on the rate of decomposition of borine carbonyl has not been shown to agree quantitatively with the rate curves (10), its qualitative agreement with the facts suggests strongly that borine molecules may have transitory existence. On the other hand, the failure to obtain any more direct evidence of the presence of borine indicates that it has too short a life to be isolated as a chemical individual.

The chemical reactions of borine carbonyl may depend in large measure upon its dissociation, or at least upon the displacement of carbon monoxide. Thus at −80°C., it is not attacked at once by trimethylamine (as diborane is), but at higher temperatures, such as would favor rapid dissociation, carbon monoxide is liberated and trimethylamine-borine is formed quantitatively:

$$H_3BCO + (CH_3)_3N \rightarrow CO + H_3B:N(CH_3)_3$$
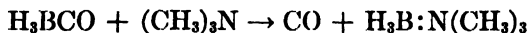
Its hydrolysis may be an even better example: it takes place according to the equation

$$H_3BCO + 3HOH \rightarrow 3H_2 + B(OH)_3 + CO$$
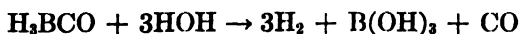
at a rate comparable to the decomposition (24), and accordingly requires heating for conveniently rapid completion. It is conceivable that the hydrolysis is not direct, but is preceded by the displacement of carbon monoxide and the formation of an unstable hydrate such as $H_2O:BH_3$. Similarly, it is possible that the hydrolysis of diborane itself involves, as a first step, the formation of such a hydrate, — an interpretation which would relate the hydrolysis of diborane to its reaction with ammonia, with amines, and with organic compounds containing carbonyl groups (5).

The reaction of borine carbonyl with ammonia, in contrast to its simple reaction with trimethylamine, is a complex process: no carbon monoxide is liberated, and the product is a non-volatile solid of composition corresponding to the empirical formula $H_3BCO \cdot 3NH_3$. This material loses one-third of its ammonia at room temperature, leaving a residue of the empirical formula $(H_3BCO)_{0.9} \cdot 2.07NH_3$. When this residue is dissolved in liquid ammonia and treated with sodium, 1 gram-equivalent of hydrogen is rapidly liberated per mole of borine carbonyl; a second equivalent of hydrogen is produced far more slowly (10). It is possible that the product of the reaction of borine carbonyl with ammonia is a mixture of two ammonium salts.

Borine carbonyl is in some respects similar to the volatile metal carbonyls (4). Like them, it agrees with Sidgwick's rule in regard to effective atomic numbers; again like them, it is more volatile than any hydrocarbon of similar molecular weight; it also shows their tendency to lose carbon monoxide reversibly, or to react with tertiary amines, with displacement of carbon monoxide. The similarities may be chiefly formal, however. In particular, it seems that borine carbonyl differs rather sharply from the hydrogen metal carbonyls.

No compounds of carbon monoxide with derivatives of borine are as yet known. Trimethylboron and the boron halides are inert toward carbon monoxide. The methyldiboranes react irreversibly with carbon monoxide, producing liquids containing neither B—H nor B—B linkages. These substances deserve further study, but they are not derivatives of borine carbonyl (17). Little is known about the behavior of the higher boranes toward carbon monoxide. The only evidence that they may react to yield carbonyl compounds is the presence of a by-product in the mixtures from which borine carbonyl is obtained. This little-known by-product is even less stable than borine carbonyl; like that substance, it loses carbon monoxide at a rate which is sharply inhibited by the presence of carbon monoxide (10).

D. Dimethyl ether-borine

The solid compound $(CH_3)_2O:BH_3$ is formed by the reaction of diborane with dimethyl ether at low temperatures (23). It is very unstable, for the reverse reaction,

$$2(CH_3)_2O:BH_3 \rightarrow B_2H_6 + (CH_3)_2O$$
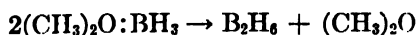
develops an equilibrium pressure of 18 mm. at $-78.5°C$. Since the compound is wholly dissociated in the vapor phase, values for its molecular weight cannot

be obtained except by cryoscopy at unusually low temperatures, and this has not yet been attempted. The formula assigned to it (i.e., $(CH_3)_2O:BH_3$ rather than $B_2H_6 \cdot 2(CH_3)_2O$) is based largely upon analogies with the behavior of diborane toward other "electron donor" molecules. In spite of its instability, the compound has proved useful in the study of the structure of the "diammoniate" of diborane, as will be described later (page 24).

Another interesting consequence of the study of the etherate (dimethyl etherborine) was the development of a method for the preparation of symmetrical dimethyldiborane, a compound not obtained by the methods used for the preparation of the other methyldiboranes. The compound is obtained by the reaction of dimethyl ether with methyldiborane at $-78.6°C$. (25). This reaction is readily understood on the assumption that, whereas dimethyl ether-borine, $(CH_3)_2O:BH_3$, is sufficiently stable to be formed at $-78.6°C.$, the corresponding derivative of monomethylborine, $(CH_3)_2O:BH_2CH_3$, is not. If this assumption is correct, the first step of the reaction is

$$B_2H_5CH_3 + (CH_3)_2O \rightarrow (CH_3)_2O:BH_3 + CH_3BH_2$$
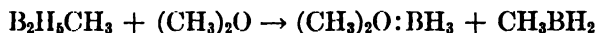
The methylborine molecules then would associate with each other to form symmetrical dimethyldiborane, $CH_3H_2BBH_2CH_3$. The success of the method which is based upon this assumption is evidence of the correctness of the latter; further evidence is found in the relative stabilities of the derivatives of trimethyl-amine-borine, described on page 17.

E. Diborane and phosphine

As is the case with its analog, ammonia, phosphine reacts with diborane in the ratio of 2 moles of the former to 1 mole of the latter (13, 23). The reaction occurs slowly at $-30°C$. in the gas phase, but more rapidly in the liquid phase at $-110°C$. (13). The compound thus formed is spontaneously inflammable in air; it is readily hydrolyzed to phosphine, boric acid, and hydrogen; it reacts rather slowly with hydrogen chloride (or bromide) at $-80°C$. to give products formulated empirically as PH_3BH_2Cl, PH_3BHCl_2, and PH_3BCl_3, although rapid disproportionation makes difficult the isolation of the individuals (13). The original compound is rather unstable (decomposition pressure, 200 mm. at $0°C.$) (13); although it can be sublimed in the high-vacuum apparatus without extensive decomposition (24), its vapor is decomposed far too rapidly for a determination of the molecular weight by vapor-density methods.

Since the molecular weight is not definitely known, there is no firm foundation on which to base hypotheses of the structure of the phosphine addition compound, but there are some suggestive experimental facts. No phosphine is liberated when the compound is dissolved in liquid ammonia at the melting point of the latter, and at $-60°C$. the evolution of phosphine is slow; in contrast to this behavior, true phosphonium salts rapidly evolve phosphine in liquid ammonia at $-77°C.$ (13). It therefore seems that the formulation $(PH_4)(H_3B:PH_2:BH_3)$, an analog to that which is favored for the "diammoniate" of diborane, would not be appropriate. On the other hand,

trimethylamine completely displaces the phosphine at $-40°C$., according to the equation

$$B_2H_6 \cdot 2PH_3 + 2N(CH_3)_3 \rightarrow 2PH_3 + 2(CH_3)_3N:BH_3$$
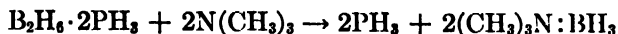
The rapid formation of trimethylamine-borine at low temperatures is a reaction characteristic of the less stable borine complexes, and consequently suggests the formulation $H_3P:BH_3$ for the compound.

The information at present available concerning the phosphine derivative is not adequate to establish definitely the structure $H_3P:BH_3$; in fact, such a structure makes necessary certain additional assumptions in order to account for the behavior of the compound toward ammonia. Unlike trimethylamine, ammonia displaces only a part of the phosphine from the compound; when the reaction occurs in liquid ammonia at $-30°C$. or higher temperatures, a fairly definite stopping point may be recognized after approximately 50 per cent of the phosphine has been displaced. The displacement may amount to 75 per cent if the ammonia is employed only in the gas phase, but there is always a remainder of phosphorus which can be recovered as phosphine only by complete hydrolysis (13). When the displacement has reached the halfway point in liquid ammonia, the solvent may be evaporated at $-60°C$., leaving a material having the empirical formula $B_2H_6 \cdot PH_3 \cdot 2NH_3$ (24). This substance loses one molecule of ammonia when pumped at $-30°C$., leaving an apparently pure substance, $B_2H_6 \cdot PH_3 \cdot NH_3$ (24). In liquid ammonia, this reacts with sodium to yield 1 gram-equivalent of hydrogen per mole of compound (13).

The fact that the mixed phosphine–ammonia compound does not liberate phosphine when dissolved in liquid ammonia or when treated with water (13) shows that it is not a phosphonium salt; its reaction with sodium suggests that it is a monoammonium salt. It is possible to reconcile this conclusion with the formulation of the original phosphinate as $H_3P:BH_3$, by assuming that this compound is transformed by ammonia into the compound $(NH_4)(H_3B:PH_2:BH_3)$. Such a reaction would be entirely analogous to the reaction which the hypothetical $H_3N:BH_3$ is supposed to undergo in order to produce the end product, $(NH_4)(H_3B:NH_2:BH_3)$, in the reaction between diborane and ammonia (see page 24).

F. Diborane and methyl cyanide

Methyl cyanide reacts slowly with diborane at $-80°C$. to form a substance of the composition CH_3CNBH_3. This is a white solid which cannot be volatilized except by dissociation, a reaction accompanied by the formation of a difficultly volatile oil. Like other complex compounds of borine, it reacts with trimethylamine to produce trimethylamine-borine, and the methyl cyanide is set free. It may be chlorinated by treatment with hydrogen chloride; this reaction is somewhat slower at $-80°C$. than the corresponding reaction of trimethylamine-borine. The compound and its products of thermal decomposition appear to be worthy of further investigation (24).

G. Diborane and pyridine

Diborane reacts rapidly with pyridine at 0°C., in the expected 2:1 ratio, to form a white solid (m.p., 11°C.) which is too slightly volatile to be handled conveniently in the vacuum apparatus. Trimethylamine displaces pyridine from the compound and produces trimethylamine-borine. Although the molecular weight of the pyridine compound has not been determined, there seems to be no reason for doubt that it is a borine derivative, $C_5H_5N:BH_3$, analogous to trimethylamine-borine (21).

V. THE REACTION OF DIBORANE WITH AMMONIA, AND RELATED TOPICS

The behavior of diborane toward ammonia is far more complex than the formation of the relatively simple addition compounds discussed in the preceding section. The various products, such as the "diammoniate," $B_2H_6 \cdot 2NH_3$, the compound B_2H_7N, and the interesting inorganic analog of benzene, $B_3N_3H_6$, themselves undergo interesting reactions, have numerous derivatives, and are suggestive of possibilities even wider than those already explored.

### A. The "diammoniate" of diborane and related compounds

Before taking up in detail the evidence concerning the constitution of the "diammoniate" -a problem having an important relation not only to the structure of diborane but also to certain questions of reaction mechanism— it is necessary to emphasize the fact that, unless the compound is prepared with particular care, it may be contaminated with by-products, the presence of which may lead to erroneous conclusions. It is obtained in pure condition when diborane is allowed to act on solid ammonia, thinly spread on the walls of a tube at −120°C., and the excess of ammonia is removed by sublimation at −100°C. A product so obtained is stable at temperatures up to +80°C., but if the procedure outlined is not closely followed, or if the temperature is allowed to rise above −80°C. before removal of the excess ammonia, the product retains more ammonia than that required by the formula $B_2H_6 \cdot 2NH_3$, and loses hydrogen at temperatures (e.g., −10°C.) at which the pure compound is unaltered. As will be shown later, these changes, resulting from departure from the procedure outlined, also produce compounds which contain more ammonium ion than does the pure "diammoniate."

The importance of these considerations is seen from an examination of the evidence adduced by Stock, Wiberg, Martini, and Nicklas (59, 60) in favor of Wiberg's formulation (62) of the diammoniate, $(NH_4)_2(H_2B::BH_2)$. These authors have studied the products resulting from the electrolysis of solutions of diborane, tetraborane, and decaborane in liquid ammonia. From a study of the gaseous products liberated at the electrodes, they conclude that two processes occur: (1) the liberation of hydrogen unaccompanied by the formation of nitrogen, and (2) the production of both hydrogen and nitrogen, a reaction which seems to be essentially an electrolytic decomposition of the ammonia used as the solvent. In a number of experiments, especially those involving diborane,

the amount of hydrogen obtained is considerably in excess of that required by the number of faradays passed through the solution. This fact indicates that secondary reactions, of the type described at the close of the last paragraph, had occurred.

The same authors have also analyzed the solid products obtained by evaporation of the ammonia after electrolysis had been discontinued. On account of the possible secondary reactions already mentioned, and because there is no evidence that the solid products were homogeneous, we do not believe that the results of the electrolysis experiments can be accepted as specifically indicating the formula $(NH_4)_2(H_2B::BH_2)$ for the diborane product, or the formulas assigned by these authors to the ammonia derivatives of other boranes. The same is true of all other evidence adduced in favor of these structural formulations (23, 60).

On the other hand, there is much evidence specifically favoring a different view: namely, that the compound is a borine complex in which two borine

molecules $\left(\begin{array}{c} H \\ H:\overset{..}{\underset{..}{B}} \\ H \end{array}\right)$ are attached to an amide ion $\left(\begin{array}{c} H \\ :\overset{..}{\underset{..}{N}}: \\ H \end{array}\right)^-$, as indicated by the

formula

$$(NH_4)H_3B:\overset{..}{\underset{..}{N}}:BH_3 \atop \text{with } H \text{ above and below}$$
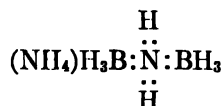
The facts and arguments leading to this conclusion may be summarized as follows (23):

(*1*) In solutions in liquid ammonia at $-77°C.$, the compound reacts with sodium (present in excess) to produce only 1 gram-atom of hydrogen for every 2 gram-atoms of boron present. Although further hydrogen may be obtained, its evolution at this point is extremely slow. It thus appears that the compound $B_2H_6 \cdot 2NH_3$ is a monoammonium salt. If the calculated amount of sodium is used, it is possible to isolate a compound having the empirical formula NaB_2H_8N, which may well be the salt $Na(H_3B:NH_2:BH_3)$.

(*2*) Trimethylamine reacts with diborane to form only the relatively simple compound $(CH_3)_3N:BH_3$, which is inert toward sodium in liquid ammonia. It seems, therefore, that it is a proton derived from ammonia, rather than from diborane, which is responsible for the formation of an ammonium ion. This deduction is in complete accord with the formulation here proposed: it is assumed

that one stage of the ammoniation involves the formation of the $\left(\begin{array}{c} H \\ H_3B:\overset{..}{\underset{..}{N}}: \\ H \end{array}\right)^-$

ion, to which a second BH_3 group becomes attached by means of the electron pair exposed by the loss of the proton.

(*3*) Evidence for the existence of the $(H_3B:NH_2)^-$ ion, mentioned in the preceding paragraph, is found in the reaction of dimethyl ether-borine, $(CH_3)_2O:$

BH_3, with sodium in liquid ammonia. If the etherate is added to a solution of sodium in liquid ammonia, 1 gram-atom of hydrogen is liberated per gram-atom of boron contained in the original etherate, and the salt $Na(H_3B:NH_2)$ may be obtained from the reaction mixture. These results are in agreement with the equation

$$NH_4^+(H_3B:NH_2)^- + Na \rightarrow NH_3 + Na^+ + (H_3B:NH_2)^- + \tfrac{1}{2}H_2$$

Furthermore, the interaction of the etherate, ammonia, and sodium, under the conditions specified, is of the first order, as would be expected if the rate-determining first step of the reaction (carried out in liquid ammonia solution) were

$$(CH_3)_2O:BH_3 + 2NH_3 \rightarrow (H_3B:NH_2)(NH_4) + O(CH_3)_2$$
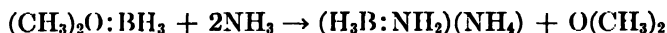
(4) There is also clear evidence of an equilibrium, represented by the equation

$$NH_4(H_3B:NH_2BH_3) + 2NH_3 \rightleftarrows 2NH_4(H_3B:NH_2)$$

When the "diammoniate" (here represented by the first formula of the equation) is allowed to remain in contact with liquid ammonia for a short time at $-40°C.$, before sodium is added, more hydrogen than corresponds to 1 gram-atom per mole of compound is liberated by the subsequent action of sodium. This result indicates that additional ammonium ions are formed, as should be observed when the reaction proceeds toward the right, approaching the equilibrium condition. If, on the other hand, the dimethyl ether-borine remains in contact with liquid ammonia for a short time before sodium is added, less than 2 gram-atoms (e.g., 1.8 or less) of hydrogen is evolved per 2 gram-atoms of boron in solution. This result indicates the reverse approach toward equilibrium,—a reaction in which $(H_3B:NH_2)^-$ ions react with ammonium ions to form $(H_3B:NH_2:BH_3)^-$ ions and ammonia.

It is also to be mentioned, in this connection, that the compound $Na^+(H_3B:NH_2)^-$ absorbs diborane to some extent, as would be expected if the $(H_3B:NH_2)^-$ ion were converted to $(H_3B:NH_2:BH_3)^-$ ion.

(5) The "diammoniate" is easily transformed into compounds which have been shown by electron diffraction and other experiments to contain a B -N—B grouping of atoms. One of these is the compound B_2H_7N (2, 29), the formation of which is discussed later; the other is the ring compound $B_3N_3H_6$, which likewise will receive further attention (pages 25 and 27).

From the point of view here developed, it is interesting that the "diammoniate" reacts with hydrogen chloride at $-80°C.$ very much in the same way as does trimethylamine-borine; the reactions proceed at similar rates (50, 25), and in both cases the reaction ceases with the liberation of 1 mole of hydrogen per gram-atom of boron, unless the temperature is raised. In both cases chlorine is substituted for hydrogen. This similarity fits in with the hypothesis that the "diammoniate" contains two borine groups, bonded as is the one in trimethyl-amine-borine. It should be noted, however, that the similarity is not a proof of structure.

Also of interest at this point is the fact that the solution resulting from the

treatment of the "diammoniate" with water possesses the same specific reducing properties (e.g., precipitation of Ni_2B) characteristic of the hypoborates obtained by partial hydrolysis of diborane in strong base solutions (50). This was interpreted as evidence that the "diammoniate" and diborane itself have similar structures; since neither the mechanisms nor the products of these partial hydrolyses are fully understood, this interpretation is not necessarily valid.

In view of the complexity of the reaction of diborane with ammonia, it is not possible to use the structure of the "diammoniate" as a valid basis for discussions of the structure of diborane itself. The study of the ammonia reaction nevertheless has thrown a great deal of light upon the more general chemical character of diborane.

B. Reactions of ammonia with the methyldiboranes

The methyldiboranes, like diborane itself, react with 2 moles of ammonia to produce solid, white, salt-like compounds (27). That they are similar in structure to the "diammoniate" of diborane is suggested by the fact that the product obtained by the action of ammonia on tetramethyldiborane reacts with sodium in liquid ammonia in the same manner (including rate and point of cessation) as does the diborane compound (24).

The "diammoniates" of most of the methyldiboranes lose hydrogen very readily. Especially unstable is the compound derived from tetramethyldiborane: even at $-35°C$. this is quantitatively transformed by the loss of hydrogen into dimethylboron amide, $(CH_3)_2BNH_2$. The same product results also from the heating of the "diammoniates" of $1,1$-dimethyldiborane or of trimethyldiborane. More stable than these is the "diammoniate" of monomethyldiborane, which can be kept for some time at room temperature without change.

C. The compound B_2H_7N

In the original publication on the reaction of ammonia with diborane at elevated temperatures (51), it is stated that the first reaction occurs according to the equation
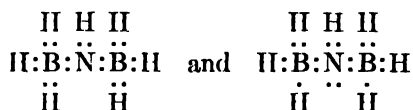
$$B_2H_6 + NH_3 \rightarrow B_2H_5NH_2 + H_2$$
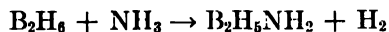
but no description of such an amide is given. Considerably later it was discovered that a substance of the composition and molecular weight corresponding to $B_2H_5NH_2$ is obtained as a by-product in the preparation of borazole (28) or, in better yields, by passing a stream of diborane over the "diammoniate" of diborane at $88°C$. and at a pressure somewhat above 1 atm. (29). But this substance, which melts at $-66.4°C$. and has an estimated boiling point of $76°C$., is not an amido diborane. Its electron diffraction (2) shows that it has a B—N—B skeleton, and that its structural pattern is closely similar to that of dimethylamine. Furthermore, 1 mole of the compound reacts with 1 mole of ammonia or 1 mole of trimethylamine to form fairly stable addition products, whereas diborane and all of its derivatives not otherwise attacked by ammonia (e.g., the alkyldiboranes) take up 2 moles of ammonia or amine.

Several different structural formulations of this compound might be considered. Most in accord with its known chemical properties is the formula

$$\text{H \quad H \quad H}$$
$$\text{H:B:N:B}$$
$$\text{H \quad H \quad H}$$
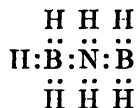
which accounts easily for the addition of ammonia or amine in the 1:1 ratio. The chief objection to this formulation is purely theoretical: the boron atom shown on the right has only a sextet of electrons, and there is no obvious means

$$\text{H}$$
of completing its octet; it thus would be similar to boron in a H:B group, and
$$\text{H}$$

accordingly might be expected to unite with another of its own kind, to form a molecule twice as large. Other formulations, however, seem less acceptable from the chemical viewpoint. Thus,

$$\text{H \quad H \quad H} \qquad\qquad \text{H \quad H \quad H}$$
$$\text{H:B:N:B:H} \quad \text{and} \quad \text{H:B:N:B:H}$$
$$\text{H \quad\quad H} \qquad\qquad \text{H \quad\quad H}$$

while implying the symmetry indicated by electron-diffraction studies (2), do not directly account for the behavior of the substance toward ammonia. The structure

$$\text{H \quad H}$$
$$\text{H:B:N\_::B:H}$$
$$\text{H \ H+ \ H}$$
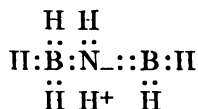
accounts easily for the addition of ammonia, but implies the presence of that all too active chemical entity, a proton bound only by electrostatic forces. On the whole, therefore, it seems as difficult to assign a specific electronic formulation to this substance as to diborane. Nevertheless, the various pictures here discussed may contribute usefully to resonance calculations of energy values.

The compound B_2H_7N is sufficiently stable to remain unchanged for several days at room temperature if out of contact with air or moisture. Over long periods of time, however, it undergoes gradual decomposition, ultimately yielding diborane, a residue of the composition $(BH_4N)_x$, and traces of other products. It is readily hydrolyzed in hydrochloric acid solution, to yield ammonium chloride, hydrogen, and boric acid. Gaseous hydrogen chloride also attacks it, evidently substituting chlorine for hydrogen, but the products have not been fully investigated.

The trimethylamine and ammonia addition products are quite stable at room temperature, but can be made to undergo interesting changes on heating. The former, when heated with excess trimethylamine, yields trimethylamine-borine and a residue of the empirical formula $BH_2N \cdot 0.5N(CH_3)_3$. Sudden heating

of the ammonia addition product to 200°C. in a sealed tube results in a 45 per cent yield of borazole.

At −60°C. the ammonia addition product liberates 1 gram-atom of hydrogen per mole of compound when treated with sodium in liquid ammonia for about 1 hr.; thereafter the reaction is very slow. At the end of the first stage of the reaction, a salt-like product of the composition $NaNH_2 \cdot B_2H_7N$ may be isolated.

D. Borazole and its derivatives

The compound $B_3N_3H_6$, already mentioned at several points in this review, has been the subject of considerable investigation and discussion in recent years. Its resemblance to benzene has led to the designations "inorganic benzene" and "borazole" (63), the latter of which we have chosen to use in the present discussion.

The discoverers of this compound (51) assigned to it the ring structure

$$
\begin{array}{c}
H-B-N-H \\
\diagup \qquad \diagdown \\
H-N \qquad\qquad B-H \\
\diagdown \qquad \diagup \\
H-B-N-H
\end{array}
$$
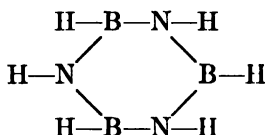
and this pattern is supported by electron-diffraction data (2, 61) as well as by the preparation of methyl derivatives (see page 29). When this structural formula is rewritten in electronic terms (I), it is seen that each nitrogen atom has an
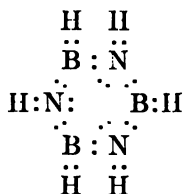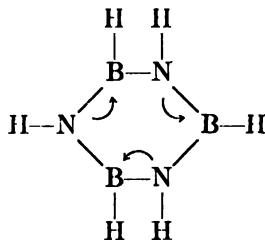
I   II

unshared electron pair, and each boron atom lacks an electron pair. Obviously the unshared electron pairs assigned to nitrogen might complete the valence shells of the boron atoms, thus creating three "internal dative bonds." The analogy with benzene then is the more striking, as shown in formula II (58, 63). Resonance undoubtedly contributes to the stability of the compound.

This formal similarity is paralleled by some rather striking similarities in the physical properties shown in table 4, which is taken from a recent discussion of the subject (63). Also very striking are the similarities in infrared and Raman spectra (12).

It is, of course, not to be expected that the chemical similarity between the two substances will be as close as the physical. Catalytic hydrogenation leads not to an analog of cyclohexane, but to an evidently polymeric material concerning which little is known. In regard to other types of addition reactions,

borazole is in general far more reactive than benzene. Thus 1 mole of borazole adds 3 moles of water, of methanol, of hydrogen chloride, of hydrogen bromide, or of methyl iodide, always yielding products which are not volatile without decomposition. Although these reactions occur with moderate rapidity, they are much slower than would be expected if borazole had the structure represented by formula I, rather than the more tightly bonded structure indicated by formula II, on page 27. Still slower and more difficult to complete are the additions of ammonia, trimethylamine, and dimethyl ether. Ultimately each is added in the ratio of 3 moles to 1 mole of borazole. The addition of the amine or the ether requires heating (60°–70°C.) and 2 weeks' time; each product is a gelatinous opaque mass (63).

It has been suggested (63) that these addition reactions may be strictly analogous to the double-bond additions of benzene chemistry, and that the more

TABLE 4

Comparison of the physical properties of benzene and of borazole

PROPERTIES	C_6H_6	$B_3N_3H_6$
Molecular weight.....	78	80
Boiling point..........	353°K.	328°K.
Melting point....................................	279°K.	215°K.
Critical temperature..............................	561°K.	525°K.
Density (liquid at boiling point)..................	0.81 g. per cc.	0.81 g. per cc.
Heat of vaporization (at boiling point)...........	7400 calories	7000 calories
Molar volume (at boiling point)..................	96 cc.	100 cc.
Surface tension (at boiling point)................	31.0 dynes per cm.	31.1 dynes per cm.
Parachor..	206	208
Carbon–carbon distance.........................	1.42 Å.	
Boron–nitrogen distance......		1.44 Å.

positive group in each adding molecule goes to nitrogen, while the more negative goes to boron. The internal dative bonds thus would be removed in favor of external bonding to both boron and nitrogen. This view seems quite reasonable for some cases, such as the addition of hydrogen halides, methyl iodide, and possibly water or ammonia. However, in the case of a molecule which is not easily split, such as trimethylamine, it seems better to assume that the intact molecule is added to boron, and the internal dative bond only suppressed. In some cases, such as that of dimethyl ether, a decision between the two interpretations is very difficult.

At temperatures from 50° to 100°C., some of these addition products lose hydrogen, forming substituted borazoles. Thus the compound $B_3N_3H_6 \cdot 3HCl$, formed by addition of hydrogen chloride at lower temperatures, yields another compound, $B_3N_3H_3Cl_3$, on heating to 100°C.; analogous results are obtained with hydrogen bromide (63). In the final products of these reactions, the halogen appears to be attached to the boron atoms of the ring.

The reactions with water and methyl alcohol proceed somewhat farther. When borazole is treated with cold water, a neutral solution is obtained; although the solute is a strong reducing agent, it is not to be confused with the hypoborate obtained by alkaline hydrolysis of diborane, for the trihydrate $B_3N_3H_6 \cdot 3H_2O$ is obtainable by evaporation of the ice-cold solution. At higher temperatures, hydrolysis sets in and ammonia is liberated; the breaking of the ring thus is clearly indicated (51).

The treatment of the trihydrate $B_3N_3H_6 \cdot 3H_2O$ with hydrogen chloride leads to loss of hydrogen and the formation of a compound of the composition $B_3N_3H_3Cl_3 \cdot 3H_2O$. A similar reaction occurs with hydrogen bromide (51, 63).

The reaction of methanol is similar to that of water; the trimethanolate is broken down by heat, yielding hydrogen and a polymeric mass, $(CH_3OBNH)_x$. This material, as well as the product of decomposition of the trihydrate, seems to form boron nitride on further heating (63).

Borazole not only forms addition compounds as just described, but undergoes ring-substitution reactions as well. Thus, both chlorine and bromine attack this pseudobenzene to produce the corresponding hydrogen halides and derivatives of the type $B_3N_3H_5X$. Unlike benzene, however, borazole does not add halogens without substitution.

The direct substitution of methyl groups for hydrogen in borazole may be accomplished by treatment with trimethylboron or with dimethylaminoborine, $(CH_3)_2BNH_2$ (28), but this procedure is not very expeditious, and replaces with methyl groups only hydrogen attached to boron. The B-methyl derivatives are more effectively prepared by rapidly heating the "diammoniates" of the mono-, di-, or tri-methyldiboranes to 200°C. in a closed tube (27). The N-methyl derivatives may be obtained by heating diborane in similar fashion with methylamine or with mixtures of ammonia and methylamine (28). The N-methyl derivatives may be further methylated by treatment with trimethylboron in a sealed tube at 100°C., yielding compounds in which methyl groups are attached not only to nitrogen but also to boron (28).

By these methods, nine of the expected methyl derivatives of borazole have been obtained, and no unpredicted derivative could be found among the products. The physical evidence favoring the ring structure (2) thus is supplemented by very strong chemical support. An ortho- and a para-N-methyl-B-methyl-borazole are theoretically possible, but only one substance of this composition has been obtained.

The physical properties of borazole and of all of its known methyl derivatives are compared in table 5.

Several mechanisms for the formation of borazole and of its methyl derivatives have been proposed. Originally it was suggested (27) that the first step in the reaction is an ammonolysis to form some derivative such as $(NH_2)H_2BBH_2(NH_2)$, which then dissociates into transitory fragments such as BH_2NH_2. Condensation of three such fragments with loss of hydrogen might then result in the formation of the ring. After the discovery that trimethylamine reacts with diborane to form a borine complex, $(CH_3)_3N:BH_3$, this hypothesis was modified

by the assumption that the high-temperature reaction with ammonia involves an analogous borine complex, $H_3N:BH_3$, which polymerizes with loss of hydrogen (23, 63). For the whole reaction, the following steps have been suggested (63):

$$3B_2H_6 + 6NH_3 \rightarrow 6BH_3 \cdot NH_3 \xrightarrow{-H_2} 6BH_2 \cdot NH_2 \xrightarrow{-H_2} 6BH{=}NH \rightarrow 2B_3N_3H_6$$

Several facts may be cited to support such an interpretation, although there is no dependable basis for deciding whether there is any ammonolysis before the B—B link is broken, or for recognizing at what point the ring formation occurs. When diborane is treated with dimethylamine, the reaction might be expected to proceed in similar fashion as with ammonia, except that only one molecule of hydrogen could be lost per borine unit, leaving the compound $H_2BN(CH_3)_2$.

TABLE 5

Physical constants of the methylborazoles

FORMULA	MOLECULAR WEIGHT		MELT-ING POINT	BOIL-ING POINT	CHARACTERISTIC VAPOR TENSOION	REFER-ENCE
	Ob-served	Calcu-lated				
			°C.	°C.	mm.	
$B_3N_3H_6$..............................	80.2	80.5	−58.0	53	85 (0°C.)	(49)
$B\text{-}CH_3B_3N_3H_5$...	94.9	94.6	−59	87*	19.5 (0°C.)	(27)
$N\text{-}CH_3B_3N_3H_5$........................	94.7	94.6		84*	23.5 (0°C.)	(28)
$B,B'\text{-}(CH_3)_2B_3N_3H_4$....................	109.3	108.6	−48	107*	6.5 (0°C.)	(27)
$B,N\text{-}(CH_3)_2B_3N_3H_4$....................	109	108.6		124*	8 (0°C.)	(28)
$N,N'\text{-}(CH_3)_2B_3N_3H_4$	109	108.6		108	8.2 (0°C.)	(28)
$B,B',B''\text{-}(CH_3)_3B_3N_3H_3$................	124.1	122.6	31.5	129*	21 (35°C.)	(27)
$N,B,B'\text{-}(CH_3)_3B_3N_3H_3$................	123.6	122.6		139	241 (100°C.)	(28)
$N,N',N''\text{-}(CH_3)_3B_3N_3H_3$...............	123	122.6		134	271 (100°C.)	(28)
$N,B,B',B''\text{-}(CH_3)_4B_3N_3H_2$........	138	136.6		158	112 (100°C.)	(28)

* This estimate came from an extreme extrapolation of vapor-tension data.

A substance of this composition, but as yet not fully described, actually has been obtained in 100 per cent yield by the reaction in question (63). Similarly, treatment of tetramethyldiborane with ammonia should and actually does lead to the compound $(CH_3)_2BNH_2$, which is incapable of further intramolecular ammonolysis; this also is obtained in quantitative yield (27). These reactions are suggestive of one stage in the suggested mechanism, but obviously throw but little light upon the rest of the process, and do not clearly account for the large yields of by-products.

When such a simple mechanism is applied to the interpretation of the reactions by which the B-methylborazoles are formed, certain difficulties arise. Thus, the reaction of monomethyldiborane with twice its (gas) volume of ammonia would be expected to produce borazole and its mono-, di-, and tri-B-methyl derivatives, in proportions represented respectively by the numbers 1:9:9:1, if it were true that CH_3BHNH_2 and BH_2NH_2 fragments combined in a random

manner. Actually, the reaction produces roughly equal quantities of borazole and its three B-methyl derivatives (27). Similar deviations from the simple theory occur also in other cases. The question whether the mechanism must be modified to include disproportionation at some stage of the process, or whether the difference is to be attributed to a selective process in the formation of non-volatile by-products, cannot as yet be decided.

VI. REACTIONS OF DIBORANE WITH ALCOHOLS, ALDEHYDES, KETONES, AND ESTERS

Diborane reacts with alcohols (9), as well as with certain compounds containing carbonyl groups (5), to form dialkoxyborines, such as $(CH_3O)_2BH$. There is evidence, especially in the case of the carbonyl type of compound, that such a reaction proceeds through the intermediate formation of a borine "complex"; for example,

$$2CH_3CHO + B_2H_6 \rightarrow 2CH_3CHO:BH_3$$
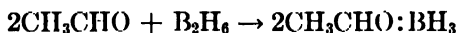
Presumably this step in the reaction is followed by rearrangement to the borine substitution derivative, - in the example cited, to $CH_3CH_2OBH_2$. By repetition of this series of reactions, the formation of the dialkoxyborine would ensue.

If this interpretation is correct, the reaction can occur only when the borine "complex" has a sufficient strength of B—O bonding. The complex must, however, not be too stable, since it must undergo rapid rearrangement. For this reason the intermediate complex cannot be isolated, but indirect evidence for the mechanism proposed was obtained through a study of the closely related addition products of boron fluoride with the organic compounds involved (5). Thus acetone, acetaldehyde, and trimethylacetaldehyde, which react rapidly with diborane even at $-80°C$., form moderately stable addition products, whereas chloral, carbonyl chloride, and acetyl chloride, which appear not to react at all with diborane, either do not react with boron fluoride, or form addition compounds so unstable that they exist only at low temperatures. Furthermore, the fact that trimethylacetaldehyde acts as readily as acetaldehyde with diborane shows that enolization is not involved in the reaction.

It is important to note, however, that esters such as methyl formate and ethyl acetate, which form especially stable boron fluoride addition products, react very slowly with diborane: there is no reaction at low temperatures, and at room temperature several hours are required to produce noticeable change. This effect is nevertheless readily explained in terms of a borine-complex mechanism. It is well known that boron fluoride forms very stable addition products with ethers. For this reason it is permissible to assume that the addition involves the ether oxygen atom, rather than the carbonyl oxygen atom, of the ester. Thus the borine complex of, for example, methyl formate, would have the structure

$$\underset{O}{\overset{H—C—O—CH_3}{\underset{\|}{}}} \quad \ddot{B}H_3$$
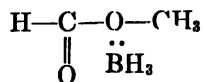
Rearrangement of this type of compound to form a borine derivative requires the rupture of a carbon–oxygen bond, a reaction presumably requiring a much higher activation energy than the wandering of a hydrogen atom (which is all that is involved in cases in which the borine is linked to the carbonyl oxygen atom).

These mechanisms involve the primary formation of monoalkoxyborines. Compounds of this type have not been isolated, but the production of unstable, solid by-products has been observed in the formation of the dialkoxyborines, and these may be polymers of the monoalkoxy derivatives. The only one of these by-products as yet subjected to study is that obtained in the reaction between methanol and diborane (9). Its composition corresponds to the empirical formula $(CH_3OBH_2)_x$. Its molecular weight has not been determined, because it is non-volatile at room temperature and slowly decomposes to yield dimethoxyborine, diborane, and methyl borate.

The compounds so far obtained by reactions of the types discussed here are the following: (a) dimethoxyborine, from diborane with methanol (9) or with methyl formate (5); (b) diethoxyborine, from diborane and acetaldehyde (5); (c) diisopropoxyborine, from diborane and acetone (5); (d) di(neopentoxy)borine, from diborane and trimethylacetaldehyde (5); and (e) ethylenedioxyborine, from diborane and ethylene glycol (24).

All but one of these (i.e., the neopentoxy derivative, having a vapor tension of only 3 mm. at 25°C.) are sufficiently volatile and stable during a long enough time to allow rapid determinations of their vapor densities. The results show that polymerization does not occur appreciably in the vapor state (5, 9). The liquids also appear to be normal, with the exception of ethylenedioxyborine, $C_2H_4O_2BH$, which reversibly forms a glassy polymer when condensed (21).

The only one of these derivatives as yet subjected to detailed study is dimethoxyborine (9). It is a moderately stable liquid (b.p., 26°C.; m.p., −130.6°C.) which decomposes reversibly according to the equation

$$6(CH_3O)_2BH \rightleftarrows B_2H_6 + 4B(OCH_3)_3$$

A rough determination of the equilibrium constant for the reaction has given the value 63 ± 5 at 25°C. (for concentrations expressed in partial pressures in atmospheres). The equilibrium mixture of diborane, methyl borate, and dimethoxyborine slowly undergoes decomposition to yield dimethyl ether, methane, carbon monoxide, hydrogen, and non-volatile solid material (24). Since methane, carbon monoxide, and hydrogen are the normal products of the thermal decomposition of dimethyl ether at red heat, the appearance of these products may be the result, either of a room-temperature, catalytic decomposition of the ether primarily formed, or of some preferential formation of the decomposition products. The reaction deserves fuller investigation.

Dimethoxyborine is not spontaneously inflammable in air, but it is readily hydrolyzed by water. With ammonia it forms an unstable addition product, $(CH_3O)_2BH \cdot NH_3$ (24).

One additional observation, made in the study of the reactions involving the

carbonyl compounds, is worthy of mention. Acetaldehyde and acetone, which react with diborane very rapidly even at $-80°C$. in the liquid state, react only very slowly in the gas phase at room temperature (5). It is not likely that the explanation of this phenomenon is to be found in a greater probability of formation of the intermediate complex in the liquid state, for other borine complexes, such as trimethylamine-borine, are readily formed in the vapor phase (24). A more likely explanation may be based upon the assumption that the unstable complexes, formed from acetone and acetaldehyde, have a longer life in the liquid phase.

VII. THE BORANE SALTS

One of the most significant reactions of diborane is its interaction with amalgams of highly active metals (sodium, potassium, calcium) according to equations (42, 44, 50, 56) such as

$$2Na(Hg) + B_2H_6 \rightarrow Na_2B_2H_6 + (Hg)$$
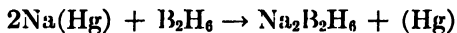
The resulting non-volatile compounds are insoluble in liquid ammonia and in the common organic solvents, and react with water; consequently the molecular formulas assigned to them are based, not upon determinations of their molecular weights, but upon their diamagnetic character (15), which rules out simpler formulas such as $NaBH_3$. That their structure is not more complex than that of diborane is a reasonable assumption, based upon an electronic interpretation of their formation.

The addition of two electrons to the electronically unsaturated diborane $(B_2H_6 + 2e - B_2H_6^{--})$ would lead to an ion having a structure analogous to that of ethane, and therefore expected to be very stable. Actually, the diborane salts are far more stable than diborane itself. The compounds $Na_2B_2H_6$, $K_2B_2H_6$, and CaB_2H_6 are so stable that all of the mercury remaining after their formation may be distilled away, leaving the purified salts in nearly quantitative yields (44, 56). The sodium and potassium salts may actually be sublimed *in vacuo* at 400°C., without complete decomposition, although as much as two-thirds of each sample is converted to free metal and to solids such as $K_2B_4H_4$ (an ill-defined substance, believed to be derived from $K_2P_4H_{10}$) (40, 44, 56). The liberation of such active metals as those here involved is in itself evidence of the strong reducing power of these compounds; this property is further demonstrated by their explosive reaction with nitric acid and their immediate reduction of permanganate.

In spite of this marked reducing power, the compounds are permanently stable in dry air at room temperature. They are, however, hydrolyzed without difficulty to produce "hypoborates," which have been shown by x-ray studies to be identical with the hypoborates produced by the action of alkalies upon diborane (3). On the basis of its diamagnetism (15), the potassium hypoborate, which originally was formulated as $KOBH_3$, has been assigned the structure $K_2(BH_2OH \cdot BH_2OH)$ and is regarded as an hydroxyl derivative of a diborane salt. In fact, like the diborane salts, these hypoborates are powerful

reducing agents: when heated *in vacuo*, they produce the free metals (and other products), and in solution, they reduce silver, bismuth, mercury, arsenic, and antimony salts to the free metals; with cupric salts they give "copper hydride" (36, 12). Their most characteristic property is the formation of a black precipitate of nickel boride, Ni_2B, from solutions of nickel sulfate.

The diborane salts are more rapidly attacked by hydrogen halides than is diborane: the reaction

$$K_2B_2H_6 + 4HBr \rightarrow K_2B_2H_2Br_4 + 4H_2$$
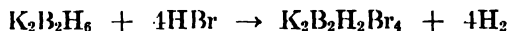
proceeds almost to completion during one day at room temperature (56). In some cases this reaction is accompanied by the production of diborane, potassium bromide, and hydrogen:

$$K_2B_2H_6 + 2HBr \rightarrow 2KBr + B_2H_6 + H_2$$
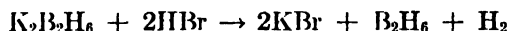
It is not certain that this reaction involves a reversal of the original preparation of the diborane salt (56).

Tetraborane and the stable pentaborane also react with alkali metal amalgams to give, respectively, $M_2B_4H_{10}$ (40, 44, 58) and $M_2B_5H_9$ (40, 44); there is some indirect evidence that tetraborane forms compounds other than the one mentioned, but the problem of their isolation has not been solved (58). The higher borane salts are less easily prepared in pure condition than is true of the diborane salts, since they lose hydrogen so readily that it is difficult to preserve them during the removal of mercury by evaporation. Thermal decomposition seems to proceed through steps which may be represented by the formulas $M_2B_4H_8$, $M_2B_4H_6$, and $M_2B_4H_4$ in the case of the tetraborane salt, and by $M_4B_{10}H_{16}$ and $M_4B_{10}H_6$ in the case of the pentaborane salt (40, 41). Although numerous interpretations might be placed upon these decomposition products, it seems best to regard them as mixtures of salts derivable from the numerous stable and unstable decomposition products of diborane. One reason for this opinion is the fact that both $K_2B_4H_{10}$ and $K_2B_5H_9$ give sublimates of potassium and of $K_2B_2H_6$ when heated to 400°C. *in vacuo*. Another reason is that during gentler heating, the tetraborane salt gives considerable proportions of diborane and the stable pentaborane, along with smaller quantities of tetraborane (40). There is thus every reason to believe that free boranes, capable of undergoing "cracking reactions," are present with the alkali metals in the initial products of decomposition.

The tetraborane and pentaborane salts behave toward hydrogen halides as do the diborane salts, except that the products are more numerous. Hydrogen, tetraborane, the stable pentaborane, diborane, potassium chloride, and non-volatile materials containing the metal, boron, hydrogen, and chlorine, all are formed by the action of hydrogen chloride (44). The potassium salt of the stable pentaborane dissolves in water without evolution of hydrogen, to give a strongly reducing solution which does not, however, give the nickel boride precipitate characteristic of the hypoborates obtained from diborane or its salts (40). It is to be noted also that this nickel test is not obtained with solutions formed by dissolving the stable pentaborane in aqueous alkali.

The existence of still other salts, formulated as $K_2B_2H_4$, $K_4B_4H_6$, and $Ba_2B_4H_6$, has been postulated, and has been used by Wiberg (62) as a part of his argument in favor of the structure $H_2(H_2B{=}BH_2)$ for diborane. But the evidence— namely, the fact that solutions containing 4 moles of sodium or potassium hydroxide or 2 moles of barium hydroxide absorb 1 mole of tetraborane without immediate evolution of hydrogen - seems inadequate as a basis for the acceptance of these formulas as representing chemical individuals.

VIII. THE METALLO BOROHYDRIDES

Among the more striking results of recent investigations in the chemistry of the boron hydrides is the discovery of metal–boron–hydrogen compounds containing unusually large proportions of hydrogen. Of these, the compounds containing lithium (20), beryllium (11), and aluminum (30, 31) have been studied most. They are prepared by the action of diborane upon alkyl compounds of the corresponding metals. Thus lithium borohydride, a definitely salt-like substance formulated as $Li^+BH_4^-$, is produced in practically pure condition by the action of diborane on solid ethyllithium at room temperature, as represented by the equation

$$2LiC_2H_5 + 2B_2H_6 \rightarrow 2LiBH_4 + (C_2H_5)_2B_2H_4$$
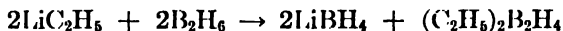
Analogous reactions produce the highly volatile, only slightly salt-like solid, beryllium borohydride, BeB_2H_8, and the still more volatile, not at all salt-like, liquid aluminum borohydride, AlB_3H_{12}. The reactions are slightly more complex than represented by the equation for the lithium compound, inasmuch as one first obtains trialkylboron compounds and, in the later stages of the reaction, mixtures of alkyldiboranes.

The physical constants of these compounds are assembled in table 6, which contains also the corresponding data for diborane for use in a comparison of the four compounds.

It is of interest to note that the beryllium and aluminum borohydrides are the most volatile compounds of these metals. Beryllium borohydride is computed to exert a pressure of at least 5 atm. before its melting point is attained, and its heat of fusion is estimated to be at least 7800 calories per mole. On sudden condensation at low temperatures, it forms a transparent glass, which changes to the white solid form at temperatures in the neighborhood of $-10°C$.

Both the beryllium and the aluminum compounds are formed only as the final reaction products of a series of reactions; other compounds, containing methyl groups, precede them in the course of the preparation, and must be used up before either of these pure borohydrides can be isolated. There are also indications that intermediates occur in the formation of lithium borohydride. The initial stage of the reaction between diborane and (solid) dimethylberyllium at 95°C. is a non-volatile, colorless, highly mobile liquid; on further treatment with diborane, this is converted into a white solid, as volatile as BeB_2H_8, but having the empirical formula CH_3BeBH_4. During the analysis of this relatively unstable compound, it was possible to show that the methyl group is attached to beryllium; the substance thus may appropriately be named methylberyllium

borohydride. This compound reacts rapidly with additional diborane to yield BeB_2H_8, along with a small amount of a non-volatile white solid which seems to be $(BeBH_5)_x$. These intermediates in the preparation of beryllium borohydride deserve further study. Also in need of further investigation are the intermediates in the preparation of aluminum borohydride; these have not yet been isolated because they are almost as volatile as the final product, aluminum borohydride.

Possibly analogous to the by-product $(BeBH_5)_x$ is a non-volatile zinc compound, $(ZnBH_5)_x$, which has been prepared by the action of diborane on dimethylzinc, but which has not been further investigated (24).

Lithium borohydride is stable in dry air, but the beryllium and the aluminum compounds inflame violently when air is allowed to enter upon them suddenly. All three compounds are readily hydrolyzed to the metal borate and hydrogen; they also react with hydrogen chloride, fairly rapidly even at $-80°C$., to yield 1 mole of hydrogen per gram-atom of boron. Diborane is liberated at the same time, and the (non-volatile) chloride of the metal is formed. On this account,

TABLE 6

Physical properties of metallo borohydrides and of diborane

FORMULA	MOLECULAR WEIGHT		MELTING POINT	BOILING POINT	CHARACTERISTIC VAPOR TENSION	REFERENCE
	Observed	Calculated				
			°C.	°C.	mm.	
LiBH₄			275(d)		Non-volatile	(20)
BeB₂H₈	38.5	38.7	>123	91.3	5.2 (at 20°C.)	(11)
AlB₃H₁₂	71.4	71.5	−65.4	44.5	119.5 (at 0°C.)	(31)
B₂H₆	27.7	27.69	−165.5	−92.5	225 (at −111.9°C.)	(36)

the action of hydrogen chloride results in an analytically useful separation of boron from the metal.

Lithium borohydride reacts with methyl alcohol to give lithium methylate and trimethyl borate; an intermediate compound, lithium boromethoxide, $LiB(OCH_3)_4$, can be isolated. The discovery of this compound led to the preparation of another compound, $LiC_2H_5B(CH_3)_3$, by the action of trimethylboron upon ethyllithium. The compound is unquestionably a mixed quaternary organoboron salt, closely related to the borohydride (20).

Of special interest in relation to the problem of the structure of the metallo borohydrides is their behavior toward trimethylamine. The lithium compound is inert to this reagent, but the beryllium and aluminum compounds form addition products and react further with the amine to liberate trimethylamine-borine. Those addition products which have been definitely isolated contain 1 mole of the amine per mole of borohydride; indications that addition products with a larger proportion of the amine may exist also have been obtained. The compound $BeB_2H_8 \cdot N(CH_3)_3$ is sufficiently stable to permit determination of the molecular weight from vapor-density measurements.

The treatment of these amine addition products with an excess of trimethylamine at slightly elevated temperatures leads to the formation of almost exactly 1 mole of trimethylamine-borine per mole of the borohydride. This removal of one BH_3 group is completed rather easily in the case of the aluminum compound; in contrast to this, the reaction of the beryllium compound is highly reversible and difficult to carry to completion. The materials remaining after the amine treatment are not as yet fully understood; they may be represented by the empirical formulas $BeBH_5 \cdot N(CH_3)_3$ and $AlB_2H_9 \cdot N(CH_3)_3$, but it is not certain that they are single substances rather than mixtures. Attempts to remove all of the boron from the compounds by use of trimethylamine, and thus to form substances which might be formulated as addition compounds of aluminum hydride and of beryllium hydride, have not been successful.

In connection with this attempt to eliminate the boron, it is of interest to note that alminum borohydride seems to form a monoammoniate by an apparently complex reaction with ammonia (31), and that by treatment of the monoammoniate with trimethylamine, as much as 93 per cent of the boron could be removed. The reaction is accompanied by loss of hydrogen and leaves a non-volatile residue; the composition of this (white) material approximates the formula $(AlH_2N)_x$. Although it is improbable that this material is an analog of borazole ($B_3N_3H_6$), it may be a compound containing an aluminum--hydrogen link. It may also be mentioned that dimethyl ether forms a 1:1 addition compound with aluminum borohydride; this compound is, however, too unstable for satisfactory study. At 60°C., it slowly produces methane (31).

On comparison of diborane with the three borohydrides thus far studied, one is struck by the fact that these four compounds constitute a series with progressive changes in properties. The gradation in physical properties from the relatively high-melting, non-volatile, essentially polar lithium borohydride to the very low-melting, very volatile, non-polar diborane is clearly shown in table 6 (page 36); it appears that aluminum borohydride approaches diborane in these respects, while beryllium borohydride is more like the lithium compound. There seems to exist also a trend in solubilities in organic solvents: aluminum borohydride is readily miscible with benzene (20), in which lithium borohydride does not dissolve at all.

A similar gradation is apparent also in the chemical behavior of these substances, a gradation most strikingly illustrated by their behavior toward trimethylamine. With this reagent, diborane rapidly produces trimethylamine-borine at −110°C.; aluminum borohydride undergoes a corresponding reaction at temperatures above 0°C., whereas the reaction in the case of the beryllium compound is not conveniently rapid at temperatures below 90°C., and lithium borohydride does not react at all. In sum, the removal of BH_3 groups (as $(CH_3)_3N:BH_3$) from these compounds becomes progressively more difficult from diborane to lithium borohydride.

On the other hand, as the ease with which BH_3 derivatives are formed decreases, the ease of formation of derivatives of the BH_4^- ion increases. Thus diborane reacts relatively slowly with ethyllithium to produce lithium boro-

hydride, whereas aluminum borohydride reacts in benzene solution by a relatively rapid reaction very similar to an ionic double decomposition (20):

$$6LiC_2H_5 + 2AlB_3H_{12} \rightarrow 6LiBH_4 + Al_2(C_2H_5)_6$$
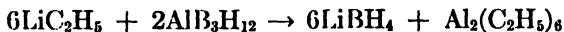
It has been suggested (20) that this gradation in properties might be explained in terms of the charge densities of the lithium, beryllium, aluminum, and boron ions. The relatively large, univalent lithium ion might be expected to exert a relatively small deforming influence on the hypothetical borohydride ion, BH_4^-. The deformation would be greater under the influence of the smaller, doubly charged beryllium ion, and still greater would be the deforming effect of the trivalent aluminum ion; greatest of all would be the deforming influence of the very small, highly charged boron ion. Consequently, whereas the lithium, beryllium, and aluminum compounds have properties which might be ascribed to the presence of the borohydride ion, although to a regularly decreasing degree, these properties have practically disappeared in the boron compound. It seems very improbable that such an aggregate as $B(BH_4)_3$ could exist; it is readily understood that extensive distortion of borohydride ion in a compound of this type would lead to disruption of that ion, and to the formation of BH_3 groups which associate to diborane.

Obviously the increasing distortion of the BH_4 group, or ion, represents a transition from the essentially ionic type of bond in lithium borohydride to the covalent type of bond in diborane. Since the latter is characterized by the electron deficiency pointed out in the introduction, aluminum and beryllium borohydrides must likewise present a degree of electron deficiency which causes their properties to approach those of diborane.

Although the beryllium and aluminum compounds are thus intermediate in character between diborane and lithium borohydride and actually possess only slight ionic properties, the names aluminum borohydride and beryllium borohydride, and the formulas $Al(BH_4)_3$ and $Be(BH_4)_2$, are both convenient and useful.

IX. CONCLUSION

The foregoing review has shown that, in spite of the difficulties inherent in work with these highly unstable, very reactive substances, considerable progress has been made. The difficulties themselves had value, in that they made necessary Stock's development of the high-vacuum methods of dealing with volatile substances,--methods which have proved extraordinarily useful whenever the necessity arose for separating small quantities of mixed volatile materials, or for studying their chemical reactions on a small scale.

The study of the boron hydrides has raised, and has brought partial answer to, new problems concerning the nature of the chemical bond, and has called the attention of chemists not only to the hydrides themselves, but also to a number of compounds such as borine carbonyl, the metal boranes, and the metallo borohydrides. These interesting new types of substances may prove useful in solving problems in related fields.

There are, however, many questions still unanswered and many facts still to be discovered. Further work is needed on the reactions of carbon monoxide with alkyldiboranes, and on the behavior of diborane toward types of organic compounds other than those which have been investigated. For example, diborane undergoes with ethylene (24) what appears to be a most unusual type of autocatalytic reaction, yielding an unusually inert solid, ethane, probably trimethylboron, and other, unidentified products. Additional work is needed to elucidate more definitely the character of the hypoborates. Further studies, some of which are now under way, are needed for a better understanding of the relationships between the various borohydrides, including those which might be formed by the heavier alkali metals, and by other metals in the second and third groups of the Periodic System. Even the problem of the structure of diborane and of the nature of its chemical bonds has not yet been completely solved. These are but a few of the many directions in which further exploration of diborane chemistry might proceed. It is, as a matter of fact, difficult to forecast the future in this field, because experience has shown that each new experiment opens up new veins, rich in interest, which could not possibly have been foreseen by analogy with the compounds of any other element.

Very important would be more development of the chemistry of the higher boranes, including the non-volatile solid products which occur in the preparation of diborane by the hydrogenation of boron halides, or which are formed in the spontaneous decomposition of diborane at low and high temperatures. Some of the volatile higher boranes have been investigated by the electron-diffraction method, as described in the review by Bauer (2), but deductions about their structure, based upon such data, must be regarded as preliminary until more is known about their chemical behavior. The chemistry of even these volatile compounds is fragmentary and not very illuminating, and practically nothing is known about the non-volatile materials. The study of their reactions with trimethylamine and with metalloörganic compounds may prove to be a promising mode of attack, but because of the instability of many of the compounds, and the complexity of the others, the problem is a difficult one which will engage workers in this field for many years.

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STRUCTURES AND PHYSICAL PROPERTIES OF THE HYDRIDES OF BORON AND OF THEIR DERIVATIVES

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CONTENTS

I. INTRODUCTION

Physical methods of investigation have proved very helpful in deducing the configurations of a number of the hydrides of boron and of their derivatives. Where such technics have been successfully applied, the spatial arrangements of the atoms within the molecules as given by the interatomic distances and bond angles are no longer in doubt; for a few compounds the force constants of the molecular vibrations as well as other physical characteristics have also been determined. The immediate problem is the assignment of electronic structures compatible with the available information.

Parallel to the conclusions based on the chemical behavior of the boron compounds, the results of x-ray and electron-diffraction studies and of absorption and Raman-spectral measurements point to interesting similarities as well as to sharp contrasts to the corresponding carbon analogs. The basic dissimilarity between the two elements is the remarkable ability of boron to participate in a

large variety of bond types; that this difference becomes evident when one compares the hydrocarbons with the boranes will be indicated below. The structural data will first be presented and discussed; electron configurations for the boranes and some of their derivatives will be suggested. Included also will be a summary of several sets of thermodynamic functions (derived from structural data on the one hand, and directly from specific heats and heats of combustion on the other), as well as the results of measurements of dielectric constant, magnetic susceptibility, and surface tension. Since the subject matter has appeared in the literature after the publication of Stock's monograph (62), it is presented in considerable detail.

II. RESULTS OF ELECTRON-DIFFRACTION MEASUREMENTS

As a tool for determinations of molecular structure the electron-diffraction method needs no justification in this review. It appears to be ideally suited for sufficiently volatile compounds which are available only in small quantities and which are not stable for a matter of days or even hours. The final structures are deduced by means of a stochastic process; to date, all conclusions have been found to be in agreement with chemical intuition, and have been repeatedly confirmed by x-ray and band-spectral investigations.

Experimental details and the various methods of reducing the data are adequately described in the reviews of Brockway (12) and of Maxwell (35). It should be noted that in an electron-diffraction study two items of information are determined,—the atomic configuration and the interatomic distances. Most of the molecules investigated had previously been assigned configurations on the basis of purely chemical data, and these have been unambiguously confirmed by the diffraction experiments; the problem was relatively simple, as it involved only the determination of the distances between atoms in the given model. For compounds in which the question of configuration had not been settled, as was the case for the boranes, the number of models which one had to consider and eliminate at first appeared tremendous. However, by limiting oneself to the known valence numbers of the elements present, and by considering their probable radii and the radial distribution curve (which is obtained directly from the photographs without reference to a particular model), one could eliminate all but a few of the conceivable configurations. The problem was thus resolved to treating in detail a small number of models by varying the interatomic distances and valence angles until (a) a particular model was found for which the computed intensity curve agreed with the one observed, both as to the qualitative appearance of the pattern and as to the quantitative positions of the diffraction rings, and (b) all the remaining models were proved unsatisfactory in spite of such variations. Only then could one state that a complete structural determination had been made.

It is clear that for the hydrides of boron, where all types of *ad hoc* linkages have been postulated, some specific while others inherently vague, it is not feasible to make a complete structural determination in the sense of (b) above. Rather than attempt to study every one of the models that have been or possibly will be proposed, the investigator considered only those atomic arrangements which appeared to him most likely, and rests his case upon the fact that the configuration he selected from among these is in complete agreement not only with the electron-diffraction data, but also with all the available physical and chemical information. Furthermore, extensive experience has shown that when the computed intensity curve for a specific model checks with the observed

pattern, it is very unlikely that a totally different model will also agree.   However, each compound should be treated individually, and safe predictions may then be made to decide whether two configurations are sufficiently unlike.   For example, with the visual method of interpreting electron-diffraction photographs, normal pentane may be distinguished from neopentane, but not readily from isopentane.

A question has often been raised as to whether it is possible to determine the positions of hydrogen atoms in a borane without the use of a rotating sector (17).   A simple computation will show that for molecules containing large numbers of *equivalent* hydrogen atoms

TABLE 1

Results of electron-diffraction studies of hydrides of boron

COMPOUND	REFER-ENCE	DEFI-CIENCY*	STRUCTURE CORRESPONDING TO†	B—B	B—H	OTHER DISTANCES
BH............	(27)	0	(Spectroscopic)		1.225	
B_2H_6...... ..	(3)	2	Ethane	1.86±0.04	1.27±0.03	
B_4H_{10}...	(6)	4	Butane	1.84±0.04	1.28±0.03	
B_5H_{11}..........	(6)	4	Pentane or iso-pentane	1.81±0.03	1.26±0.03	
B_5H_9.........	(7)	4	Methylenecyclo-butane	1.76±0.02	1.17±0.04	
H_3BCO........	(4)	0	Ketene		1.20±0.03	B—C = 1.57±0.03 C—O = 1.13±0.03
$(CH_3)_3N:BH_3$.	(4)	0	Neopentane			B—N = 1.62±0.15 N—C = 1.53±0.06
B_2NH_7........	(5)	2(?)	(Dimethylamine)		(1.20)	B—N = 1.56±0.03
$B_3H_3H_6$........	(5, 65)	0	Benzene			B—N = 1.44±0.02
$Al(BH_4)_3$.....	(9)	6	Trivalent aluminum, planar; boron in trigonal bipyramid		1.27±0.04	Al—B = 2.14±0.02

* This column refers to the "electron deficiency" of the molecule, defined as twice the number of valence bonds minus the number of valence electrons.

† This column gives the structural type.

this is quite possible.   Thus, for a hydride of boron represented on the average by n BH_2 groups, the scattered electron intensity is essentially determined by the following terms:

$$I(s) = 12n \frac{\sin as}{as} + 24(n-1) \frac{\sin bs}{bs} + 25(n-1) \frac{\sin cs}{cs} + 25(n-2) \frac{\sin ds}{ds}$$

$$+ \text{ terms involving distances greater than } d$$

where a = boron-hydrogen distance,

c = boron-boron distance,

$b = \sqrt{a^2 + c^2 + 0.666ac}$ (assuming tetrahedral valence angles), and

$d = 1.633c$ (assuming tetrahedral valence angles).

Clearly, the first two terms which involve the boron-hydrogen distance are almost as important as the subsequent ones, so that it is feasible to fix the positions of the hydrogen atoms in this manner.

Once the atomic configuration is established, the interatomic distances may be obtained

to an accuracy which depends on the complexity of the molecule and the patience of the observer (12, 35, 67). The most recent calibration of the visual method of interpreting electron-diffraction photographs has been undertaken by Schomaker and Stevenson (57); they found that in favorable cases an accuracy of 0.5 per cent is possible (comparison made with values deduced from band-spectra measurements). Because of the low atomic number of the scatterers, considerably larger limits of error have been assigned to the interatomic distances quoted for the boranes; the limits given are, however, on the conservative side.

In table 1 the results of electron-diffraction studies of several hydrides of boron are summarized.

The simplest of the hydrides has only spectroscopic stability. It is analogous in many respects to the diatomic hydrides of carbon and nitrogen; the interatomic distance quoted was deduced from its moment of inertia. Concerning the next three hydrides, it was stated above that many of the structures previously suggested (70) do not correspond to a definite geometric form and hence were not considered in detail. It soon became clear that, for diborane, an ethane-like model with the ratio B—B/B‑H = 1.47 was in good agreement with the data[1]; B_4H_{10} and B_5H_{11} presented a similar case. For the latter compound the photographs were not sufficiently good to permit distinguishing between a pentane-like and an isopentane-like configuration. A point of interest with regard to internal rotation may be mentioned here. Although electron-diffraction photographs definitely eliminate rigid configurations for B_4H_{10} and B_5H_{11}, they cannot be used to determine whether a restricting potential of several kilocalories or complete freedom of rotation exists about the B —B bonds. However, the configuration of B_5H_9 is somewhat strange, were one to reason by analogy from the corresponding carbon compounds. Whereas the cyclobutanes are less stable than their aliphatic chain analogs, this pentaborane, as well as hexaborane and decaborane, differ from the other hydrides in that they form a group of relatively greater stability. To provide further confirmation of the structure given in the table for B_5H_9, electron-diffraction photographs of methylenecyclobutane were taken (8). The form of the pattern was found to be identical with the one for the pentaborane except in the shape of one peak,

[1] In the original investigation (3) only ethane-like and ethylene-like (70) models were studied. The large B—B/B—H ratio definitely eliminates the latter, for which a value near 1.35 is to be expected. Very recently, interest in the configuration wherein two hydrogen atoms form a bridge between the boron atoms (18, 15) was again revived, with the
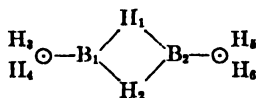
$(B_1H_1H_2B_2$ in a plane perpendicular to the plane of $H_3H_4B_1B_1H_5H_6)$

hope that it would provide a simple explanation for the rather complex infrared spectrum observed by Stitt (61). The question then arose whether the electron-diffraction data contradicted such an assumption. Intensity curves were computed for this model for various B—B/B—H ratios and boron valence angles. Only by assuming distorted bond directions ($<H_1B_1H_2 = 100°$, $<H_3B_1H_4 = 120°$, and B—B/B—H = 1.79/1.18) could agreement be obtained between the predicted and observed intensity of electron scattering for values of s_0 between 4.5 and 20. However, this bridge model *fails* to predict the appearance of a small inner peak at about $s_0 = 3$, as is observed on both the diborane and the ethane photographs, and hence can be eliminated. The results of several other experiments lead to the same conclusion; these will be discussed in detail below.

just as predicted from the computed curves. It has been suggested (7) that B_6H_{10} has a dimethylcyclobutane-like structure, and that the configuration of $B_{10}H_{14}$ is a double four-membered ring with BH_3 groups at the two ends:
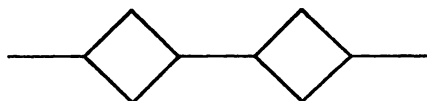
In borine carbonyl the B—C—O atoms are linearly arranged, with boron tetrahedrally bonded to three hydrogens and a carbon. However, the compound B_2NH_7 requires further elucidation; there is still some doubt whether its configuration is $H_3B:NH:BH_3$, as in dimethylamine, or $H_2B:NH_2:BH_3$. Schlesinger and coworkers (54) give several arguments, based on the chemical behavior of the substance, which favor the second of the two atomic arrangements; all but one (the fact that only one molecule of ammonia is added with the formation of a B—N link) may be equally well accounted for by the first, assuming resonance between several Lewis structures, as will be discussed below. The electron-diffraction data strongly support the dimethylamine-like configuration, but do not definitely eliminate the second, provided both boron–nitrogen distances are assumed equal. The structure of $B_3N_3H_6$ is analogous to that of benzene.

The structure of AlB_3H_{12} can best be represented diagramatically as shown in figure 1.
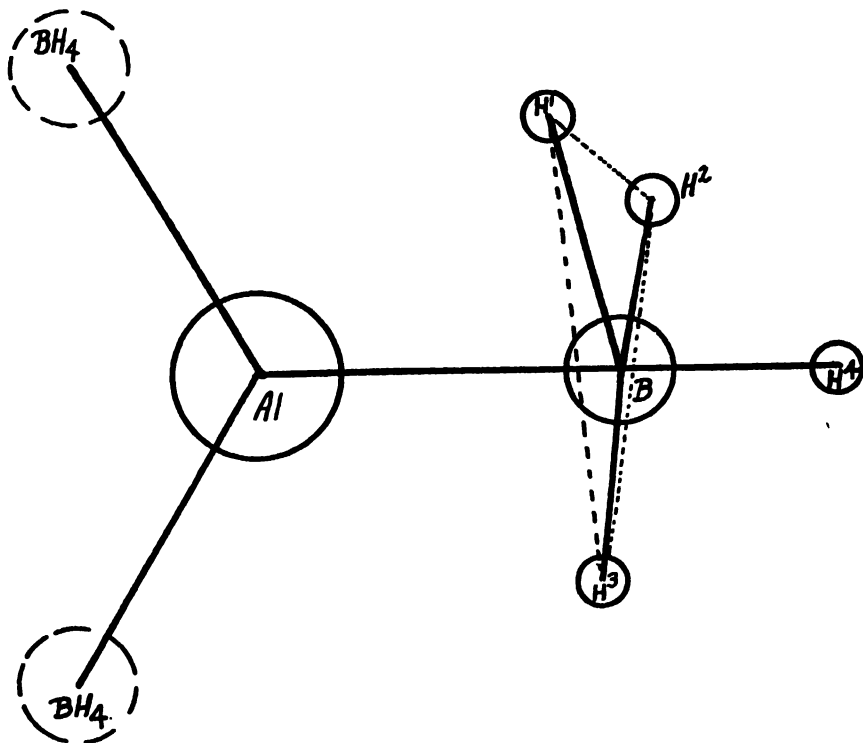
FIG. 1. $Al(BH_4)_3$

$$\angle AlBAl = 120° \qquad \angle AlBH^2 \text{ (or } H^1, H^3) = 85° \qquad \angle AlBH^4 = 180°$$

The boron atom is not quite at the center of an asymmetric trigonal bipyramid; the steric requirement that non-bonded hydrogen atoms (H^4 and H^1, H^2, H^3) be approximately 2 Å. apart forces the $\angle AlBH^1$ to be less than 90°. The available chemical data (55), although meagre, are in harmony with the above arrangement of atoms. The structures of the other metallo borohydrides (BeB_2H_8 and $LiBH_4$) are very likely analogous to that of the aluminum compound (14, 53).

III. RESULTS OF X-RAY STUDIES OF CRYSTAL STRUCTURE

As yet, no complete structure determination has been made of crystals of any boron hydride or of a derivative. Powder photographs of diborane at liquid-air temperatures have been taken by Mark and Pohland (34). These investigators found a complete similarity between the structures of ethane and

TABLE 2

Results of x-ray studies of crystal structure

	B_2H_6	C_2H_6
a	7.89 Å.	7.74 Å.
b	4.54 Å.	4.46 Å.
c	8.69 Å.	8.19 Å.
c/b	1.91 Å.	1.84 Å.
n	4	4
X—X (in molecule)	1.8–1.9 Å.	1.5–1.6 Å.
Distance between axes of adjacent molecules	4.54	4.45
Volume per molecule in lattice	78.0 Å.³	70.6 Å.³

of diborane. In both cases the crystals are hexagonal; the space group is D_{6h}^4, with four molecules per unit orthohexagonal cell.

To place the boron (or carbon) atoms, only one parameter had to be determined. The final results of this study are given in table 2. Even though the hydrogen atoms could not be located, the close parallel between the two unit cells strongly indicates a similar disposition of the hydrogen atoms in ethane and in diborane.

Möller (36) worked with single crystals of decaborane. He reported that the crystals are rhombic bipyramidal and that the space group is V_h^{21}, with two molecules per unit cell: $a = 14.46$ Å., $b = 20.85$ Å., $c = 5.69$ Å. He was further able to demonstrate that the molecules must have one of the following symmetries: C_i, C_2, or C_s. Hence he concluded that, if $B_{10}H_{14}$ is a chain, it must be strongly bent or folded; a more reasonable proposal presented by Möller is that the compound has a double-ring structure analogous to that of naphthalene; the structure suggested by Bauer and Pauling (7) is another possibility.

Debye–Scherer photographs of a number of salt-like compounds of alkali metals with these hydrides have been published (10, 63). The crystals thus

studied are $Na_2B_2H_6$, $K_2B_2H_6$, CaB_2H_6, $K_2B_4H_{10}$, $Na_2B_4H_{10}$, and $K_2B_5H_9$. Very little data are given in the reports. Since analyses have not yet been offered by the investigators, a number of interesting problems are thus open to those working on crystal structure.

IV. DEDUCTION OF ELECTRONIC CONFIGURATIONS FROM MOLECULAR STRUCTURES

From the above structures and other physical data it is possible to deduce a number of interesting conclusions regarding the electronic configurations of the boranes. However, to establish a common basis for discussion we shall summarize briefly two well-established points.

A. Even when electron configurations are known as well as we may ever hope to know them, as is the case at present for atoms, diatomic molecules, and a few polyatomic molecules, the concept is essentially an approximation. To a greater or lesser extent, the electrons belong to the molecule as a whole and there are continual exchange interactions between them, but the approximation of assigning given numbers of electrons to particular orbitals is a fairly good one for the inner-shell (atomic) electrons, and is a convenient book-keeping scheme, though perhaps not a rigorous one, for the valence (*atomic* or *molecular*,—depending on the point of view) electrons. Clearly, it is not advisable to localize valence electrons too specifically.

B. There are two methods of approach to the problem of the distribution of valence electrons in a molecule (68). In the zero-order approximation of the atomic orbital scheme, all electrons are placed in somewhat modified atomic orbits but every valence electron is permitted to occupy one orbital in each of two adjacent atoms, -these orbitals being so chosen that the density of electricity extends in the direction of the bond. (An *atomic orbital* is defined as a one-electron wave function for an electron moving in the field of only one atom.) To form an electron-pair bond there are needed two electrons with opposed spins and a stable orbital in each of the two bonded atoms. The Lewis electron-pair bond is thus incorporated in quantum-mechanical discussions of valence. However, many molecules, among them the boranes, cannot be simply represented by atoms attached to one another by Lewis bonds. To them it may be possible to assign more than one Lewis structure and, as a consequence, some of the bonds are single in one configuration, double or triple in another, etc. Since the ground state of the molecule is best represented by a linear combination of all the structures which possess the same symmetry, this combination having an energy lower than any of the component terms, it is customary to speak of the individual bonds as being a given fraction single, double, or triple.

In this review we shall refer only occasionally to the alternative point of view of assigning electron configurations by the method of molecular orbitals. The latter emphasizes the fact that the valence electrons occupy orbits which are characteristic of the molecule as a whole; thus, a *molecular orbital* is defined as a wave function which gives the probability density of only one electron and which is a solution of the dynamical problem involving all the nuclei and that electron, corrected for internuclear repulsions. Hence it is highly dependent on the symmetry of the atomic arrangement. A symbolism has evolved as a consequence of group theory considerations of the symmetry properties, but the final assignment of electrons to the various possible orbitals is based on a comprehensive study of the spectra, electric and magnetic susceptibilities, and ionization potentials and on a correlation of the energy levels of the whole ensemble of atoms with those of the smaller units comprising the molecule. Since the wave function for the whole molecule (containing n electrons) is approximated by a product of n molecular orbitals, the assignment of integral numbers to bonds becomes somewhat nebulous; the degree of "bonding," "non-bonding," or "anti-bonding" character exhibited by the electrons in a particular orbital varies with the atoms involved.

In spite of the fact that in some instances (i.e., in the discussion of hyperconjugation in methylacetylene and ethane (45)) the molecular-orbital description appears to be the less artificial of the two, the atomic-orbital method is the more familiar one to chemists.   We shall therefore discuss the electron configurations of the hydrides of boron in terms of resonance among several Lewis structures and shall but briefly present the molecular-orbital configuration for diborane.   Our approach is based on the assumption that the bond distance is a function of the density of bonding electrons between the atoms.   Pauling and coworkers (46) were first to point out that a definite relation existed between *bond order* and the distance between adjacent atoms, the form of which depends
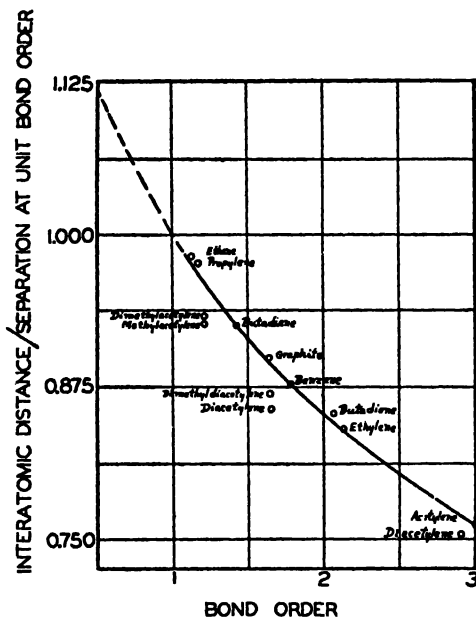
Fig. 2. The interatomic distance, with that for single bond taken as unity, is plotted along the ordinate and the degree of multiple bonding along the abscissa.   C—C pure single bond = 1.58 Å., extrapolated.   According to Mulliken *et al.*

on the definition selected for the term "bond order."   For instance, one may compute for each bond in a molecule an order number by summing over all the electron pairs contributing to the bond, each weighted by the probability of its being at the bond under consideration.   A recently published curve[2] for C—C bonds is reproduced in figure 2 (45).   We have extrapolated the curve (dotted portion) towards the left, to bond orders less than unity; clearly, the interatomic distance would be greater when part of the time only one electron or no electrons occupied the orbitals forming the bond between adjacent atoms (46, Chapter VIII).   (Compare, for instance, H_2, $r_e = 0.749$ Å., $D_e = 4.454$ volts

[2] Similar curves have been published by Lennard-Jones and Caulson, Penney, and others.   For further discussion and references see 45.

(electron-pair bond), with H_2^+, $r_e = 1.070$ Å., $D_e = 2.62$ volts (one-electron bond).) Parallel to the dependence of bond distance on bond order, relationships between the interatomic distance, the force constant for the stretching vibration, and the energy of dissociation of the bond have been proposed (33). It is reasonable to postulate that curves of the general form shown in figure 2 are applicable to pairs of atoms other than C—C. If, for a given pair, a single point on the curve is determined (such as the separation corresponding to unit bond order), one may thenceforth use it either to predict interatomic distances from computed bond orders or to deduce bond orders from observed distances, providing certain small corrections are applied to the distances between atoms, these being due to factors such as the extent of s-p hybridization (which is assumed to account for some points falling below the curve, in figure 2), the presence of formal charges, change in coördination number, forces between non-bonded atoms, etc.

After a study of many compounds, Pauling and Huggins (48) proposed a table of atomic radii; the sum of these radii for a given pair of atoms was the separation expected when they were held together by a single bond. According to this first approximation, the extent of the ionic contributions to the ground state of the molecule did not exert an observable influence on the interatomic distances. Recently a more successful procedure for predicting the interatomic distance for a given pair of atoms at unit bond order was proposed by Schomaker and Stevenson (56), in which the difference in electronegativity between the two atoms and thus the ionic character of the bond were taken into consideration. Their equation is

$$d_{AB} = r_A + r_B + \alpha \,|\, x_A - x_B \,|$$

where $\alpha = -0.09$, r_A and r_B are the tabulated radii (which differ somewhat from the values of Pauling and Huggins), and x_A and x_B are the positions of the atoms in Pauling's electronegativity table (46). Still better approximations may be proposed; in fact, R. S. Mulliken suggested that an expansion of the form

$$d_{AB} = r_A + r_B + \alpha_1(x_A - x_B)^2 + \beta_1(x_A - x_B)^4$$

has a more valid theoretical basis than the one given above. Regardless of the equation used, however, it is clear that, given an appropriate table of radii and values for the constants α and β, one can deduce from figure 2 the bond orders of various interatomic linkages when the corresponding interatomic distances are known. From these bond orders, a fair notion of the electronic configuration of the molecule can be obtained.

V. THE INTERATOMIC DISTANCES EXPECTED IN THE HYDRIDES OF BORON

As was pointed out in the introduction, one finds that boron enters into a wide variety of bonds, showing coördinations of 3, 4, and 5, with 4 as the most usual number. Previous to the suggestion of Schomaker and Stevenson (56), the observed interatomic distances for compounds of boron appeared to fall into two groups, those leading to a covalent radius of 0.88 Å., and those which could

be satisfactorily accounted for only by assuming a radius close to 0.80 Å. Bauer and Beach have discussed this question (8) and have found that the difficulty is almost completely removed when the electronegativity difference between the atoms is taken into consideration. It is, therefore, instructive to compare table 1 with table 3.

The particularly large values observed for B—B *and* B—H *in* B_2H_6, B_4H_{10}, B_5H_{11}, B_5H_9, *and* $Al(BH_4)_3$ *lead to the supposition that in these molecules the bonds are of order less than unity; i.e., these bonds are weaker than single covalent ones,* as may be deduced from the upper extrapolated region of figure 2.

TABLE 3

Interatomic distances expected in boron compounds

ELEMENT	RADIUS	BOND	INTERATOMIC DISTANCE EXPECTED*
			Å.
B................................	0.85	B—B	1.70
H................................	0.37	B—H	1.21
C................................	0.77	B—C	1.57
N................................	0.74	B—N	1.50
Al..........	1.28	B—Al	2.08

* Schomaker and Stevenson.

VI. ELECTRONIC STRUCTURES OF THE HYDRIDES

A. *Boron hydride,* BH

The electron configuration of the diatomic hydride has been given by Mulliken (37) in terms of molecular orbitals; the ground state is best represented by

$$BH: \quad (1s_B^2)(2s\sigma)^2(2p\sigma)^2, \quad {}^1\Sigma^+$$
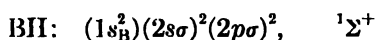
Three excited states are known—${}^3\Pi$, ${}^1\Pi$, and ${}^3\Sigma^+$—produced by raising the $(2p\sigma)$ electron to the higher $(2p\pi)$ state, but the equilibrium interatomic distances change little in going from one to the other. Values of the exchange integrals by means of which the energy of the hydride molecule may be expressed have been discussed and summarized by King (27).

B. *Diborane,* B_2H_6

That both the B—B and B—H bonds in diborane would be of order less than unity was to be expected on the basis of the electronic structures suggested by Sidgwick (58) and Lewis (32); the proposed configurations have been discussed by Pauling (47) and Mulliken (42). Sidgwick's structure (formula I, below) gives each B—H two-thirds single-bond and one-third one-electron-bond character; hence the large B—H separation. A slight extension of this configuration considering resonance to structures such as II would further account for the observed increase in the boron–boron distance. The electron-diffraction data are equally compatible with Lewis' electron configuration, representing

resonance among the seven structures III and IV, giving each bond six-sevenths single-bond character and one-seventh no-bond character (i.e., each bond orbital is unoccupied, on the average, one-seventh of the time).

In the language of atomic orbitals, the electron configuration of diborane should therefore be described as follows: The allowed orbitals for boron are four in number, of the hybridized sp^3 type, directed toward the corners of a tetrahedron. Each of these may be occupied by a shared electron pair or by a single electron, or may be left empty. Thus the valence-bond configurations which contribute to the ground state are (formal charges indicated):

$$
\begin{array}{cc}
\text{H}\quad\text{H} & \text{H}\ \text{H} \\
\text{H}^{+1}\!\cdot\ddot{\text{B}}^{-1}\!\!:\!\ddot{\text{B}}^{-1}\!\cdot\text{H}^{+1} & \text{H}^{+1}\!\cdot\ddot{\text{B}}\cdot\ddot{\text{B}}^{-1}\!\!:\!\text{H} \\
\ddot{\text{H}}\quad\ddot{\text{H}} & \ddot{\text{H}}\ \ddot{\text{H}} \\
(9) & (6) \\
\text{Type I} & \text{Type II}
\end{array}
$$

$$
\begin{array}{cc}
\text{H}\quad\text{H} & \text{H}\quad\text{H} \\
\text{H}\!:\!\ddot{\text{B}}\quad\ddot{\text{B}}\!:\!\text{H} & \text{H}^{+1}\ddot{\text{B}}\!:\!\ddot{\text{B}}^{-1}\!\!:\!\text{H} \\
\ddot{\text{H}}\quad\ddot{\text{H}} & \ddot{\text{H}}\ \ddot{\text{H}} \\
(1) & (6) \\
\text{Type III} & \text{Type IV}
\end{array}
$$

and

$$
\begin{array}{c}
\text{H}\quad\text{H} \\
\text{H}^{+1}\!\cdot\ddot{\text{B}}\ :\ \ddot{\text{B}}^{-1}\!\!:\!\text{H} \\
\text{H}^{+1}\ \ddot{\text{H}} \\
(6) \\
\text{Type V}
\end{array}
$$
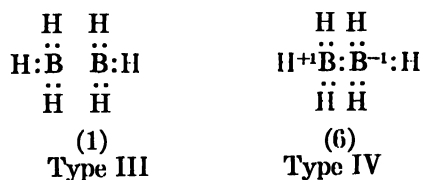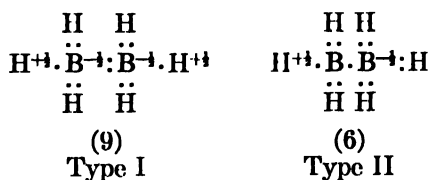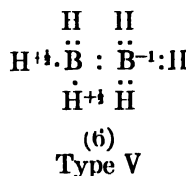
so that the wave function of diborane may be represented approximately by a linear combination of the wave functions of the above structures.[3] Although the individual members of the types II, IV, and V do not have the symmetry which we associate with diborane (D_{3d}), symmetric and antisymmetric linear combinations of the various components of each type (given in parentheses below the structures) will result in two configurations of equal energy, one of which (the symmetric) may be used in further combinations with I and III. The latter interaction will cause the energy of the over-all symmetric combination to be lowered, and of the remaining antisymmetric one to be raised,

---

[3] Justification for writing the configurations involving a one-electron bond between B_2H_5 and H, as in structure I, has been presented by Pauling (47); a similar argument may be given in favor of structures involving a one-electron bond between two BH_3 groups (3).

It is clear that the total of twenty-eight structures suggested for diborane are not independent; however, the selection of a suitable independent set should await an attempt at a quantitative discussion.

so that the ground state of diborane will be of the A_1 type. To deduce the multiplicity of the ground state consider the following: Structures III and IV are in singlet states; structures I, II, and V may have the spins of the electrons participating in the one-electron bonds either parallel or antiparallel, but only when in the latter configuration are the structures permitted to combine with III and IV. Since such an interaction will lead to a lowering of the energy of the ground state, we may conclude that the latter is singlet, i.e., that diborane has a ground state which is diamagnetic ($^1A_1$), as observed, and a low-lying paramagnetic state ($^3A_2$), the existence of which has not yet been verified.[4]

Mulliken (42) has presented a discussion of diborane and related molecules in terms of molecular orbitals. He has listed the possible electron configurations which combine to form the various states of diborane, and a rough correspondence between these and the atomic-orbital representations given above has been indicated (3). Of particular interest is the tentative energy-level scheme proposed by him, showing how the various electronic states of two BH_3 radicals correlate with those of diborane. These estimates are based in part on an analogy with the states of molecular oxygen, which is isoelectronic with diborane, and were intended to indicate orders of magnitude only. In figure 3 the levels on the right are those of two BH_3 groups, with the electron configurations of the various states indicated. Those on the left are the lower ones of diborane; five levels ($^3A_{2g}$, ^1E_g, $^1A_{1u}$, ^3E_u, and $^3A_{2u}$, in order of increasing energy) are represented by the bracket. Only $^1A_1$ states contribute to the ground level, and the two participating to the greatest extent are shown. The dotted horizontal lines are the estimated positions of these $^1A_{1g}$ states had they not interacted; mutual perturbations pushed them apart, as shown by the arrows. Dissociation correlations are indicated by the sloping lines, assuming that the symmetry D_{3d} is preserved during the dissociation. In considering the possible electronic transitions, Mulliken concluded that, since the transitions which are permitted for selected angles of orientation of the two BH_3 groups will probably

---

[4] Were one to overlook the discrepancy between the intensity curve predicted on the basis of the bridge model[1] and the pattern observed, comparison of the dimensions required for such a configuration (B—B = 1.79 Å.; B—H = 1.18 Å.) with table 3 will call attention to an inherent structural difficulty. Since the separation expected for a B—B single bond (1.70 Å.) is only slightly less than that required for the bridge model, one would have to use the following valence-bond structure
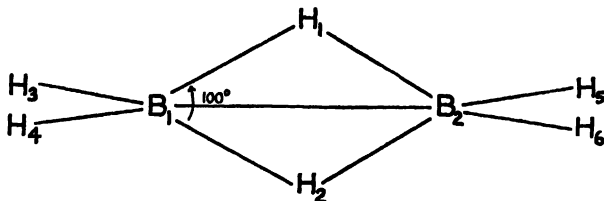
in order to represent the structural data even partially. Not only is a high electron deficiency thus introduced, but one must also postulate a pentavalent boron atom with three of its bonds coplanar and making an angle of 50° with one another, an absurd conclusion.

be weak, whereas the ones between singlet and triplet states are forbidden in light molecules, the transition which would be fairly intense and easily observed is $^1A_{1g} \rightarrow {}^1E_u$; it should be found in the near infrared. Also, the paramagnetic $^3A_{2g}$ state should make its presence evident by introducing a paramagnetic con-
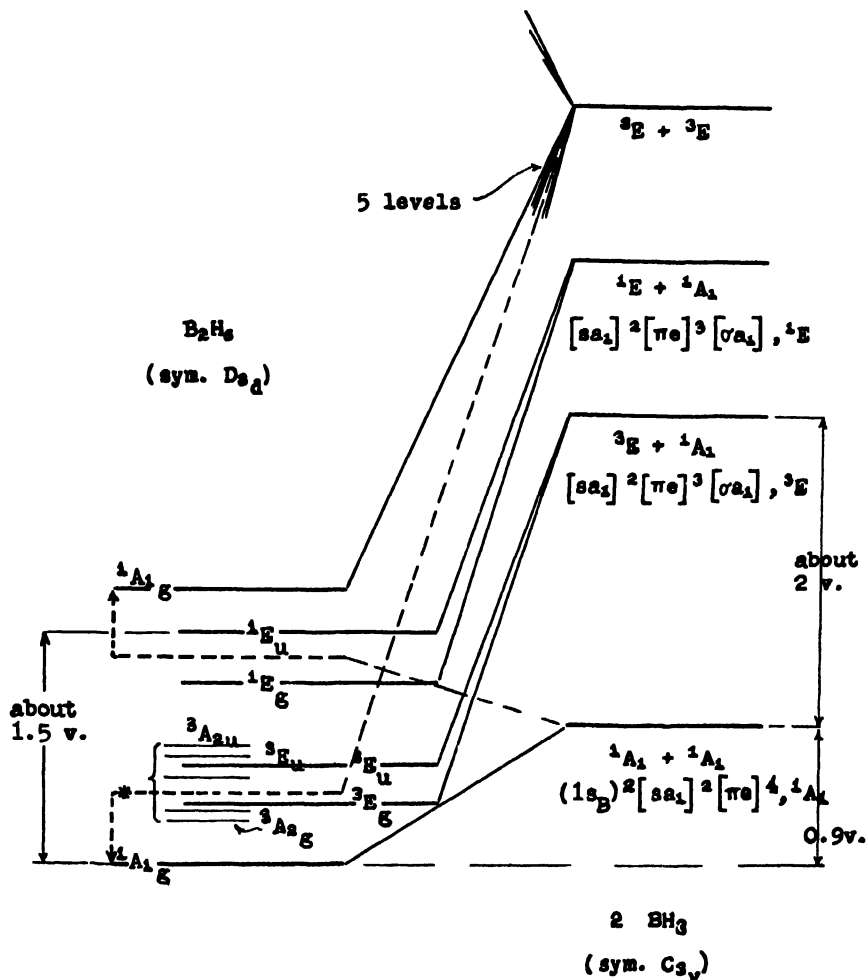
FIG. 3. Diagram showing how the energy levels of diborane may be correlated with those of two BH_2 groups (according to Mulliken).

tribution to the susceptibility as the temperature is raised. The data regarding these predictions will be presented below.

As an example of the electron configurations describing the left-hand set of levels, we quote

$$[s + s, a_{1g}]^2[s - s, a_{2u}]^2[\sigma + \sigma, a_{1g}]^2[\pi e]^3[\pi e]^3, {}^1A_{1g}, \text{ etc.}$$

for the state marked by *; it corresponds to structure I, above. One should note that whole-molecule orbitals are written for the $[sa_1]$ electrons, but not for the $[\pi e]$ electrons.

The use of whole-molecule orbitals $[\pi + \pi, e_u]$, $[\pi - \pi, e_g]$ would indicate strong resonance between the $[\pi e]$ electrons of the two BH_3 groups. This would necessitate that the $[\pi]$ bonding be strong, and that there be considerable overlapping of their wave functions in the region between the boron atoms, introducing effectively a double-bond contribution. Each of the BH_3 groups would then have a tendency to be planar. The observed spatial structure is in contradiction to such an hypothesis. The boron–hydrogen and the boron–boron distances are larger than might have been expected even for pure single bonds, and the BH_3 groups are pyramidal. (Wiber's structure (70) is therefore eliminated.) Indeed, this state of affairs was anticipated by Mulliken on the basis of the fact that diborane does not have an absorption region in the visible. The possibility of a slight double-bond contribution, both in diborane and in ethane, should be retained, however (estimated at roughly 12 per cent for the latter). In the former, the shortening thus introduced would be more than counterbalanced by the Sidgwick and Lewis structures. It has been estimated (44) that the magnitude of this effect (hyperconjugation) is too low to account for the observed barrier height restricting freedom of rotation about the C—C and B—B single bonds.

Professor Mulliken also called attention to the theorem discovered by Jahn and Teller (24), namely, that the degenerate states of most symmetric polyatomic molecules are unstable, in such a way as to cause the molecules to become less symmetric, with the consequent splitting of these states into non-degenerate ones. These forces which would tend to introduce into diborane a symmetry lower than D_{3d} are strongest for levels with orbital degeneracy (such as ^1E), particularly when the degenerate electrons participate in the bonding. However, the final configuration of the two components of the split ^1E_u state may not differ appreciably from the normal-state configuration.

C. Extension of the theory to B_4H_{10} and B_5H_{11}

The extension of the hypothesis of resonance between various electronic structures, involving electron-pair, one-electron, and no-electron bonds, to B_4H_{10} and B_5H_{11} is based on the assumption that a structure involving a one-electron-bond or no bond between two boron atoms has a somewhat higher energy than one with those bonds between a boron and hydrogen atoms (owing to the slightly greater electronegativity of boron with respect to hydrogen); hence it contributes less to the ground state. As the number of atoms in the molecule increases, the B—B links tend to be more fully covalent at the expense of the B—H bonds, resulting in a boron–boron separation closer to that expected for a pure single bond. It appears likely that the configuration of B_5H_9 may be represented by a linear combination (7) of
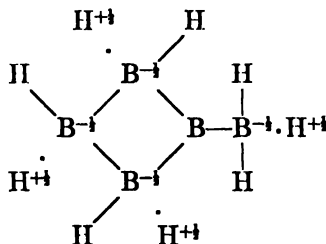
and the structures resulting from the permutation of the four one-electron bonds (and possible no bonds) among all the linkages in the molecule. The distances between the boron atoms are approximately 0.05 Å. less in B_5H_9 than in B_5H_{11},

in spite of the fact that both molecules have the same four-electron deficiency; this may be associated with the relatively greater stability of the hydride, though it is not clear why a four-membered ring should be particularly stable.

D. Borine carbonyl, H_3BCO

Let us now consider the electron configurations of the derivatives in terms of their interatomic distances.   In borine carbonyl the B—C—O atoms are linearly arranged, with the carbon–oxygen separation very near to that in carbon monoxide.   The fact that the compound readily dissociates into carbon monoxide and diborane at room temperature further supports the assumption that the characteristic resonance of the carbon monoxide molecule (39)

$$:C^-:::O^+:   \quad :C::O:: \quad :C^+:\overset{..}{\underset{..}{O}}^-: $$
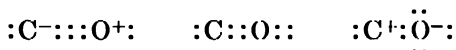
has not been quenched in the association of the latter with the BH_3 group.   The substance is gaseous at fairly low temperatures (vapor pressure 314 mm. at $-78.8°C$.) and thus probably has a low dipole moment.   Finally, one should note that in borine carbonyl, conjugation of the type found in methylacetylene is possible (first-order hyperconjugation), as contrasted with $(CH_3)_3B$ and $(CH_3BO)_3$, wherein second-order hyperconjugation is permissible (45).

In terms of electron-pair-bond structures, the ground state resonates among the following (4),

$$
\begin{array}{cc}
\text{H} & \text{H} \\
\text{H}:\overset{..}{\text{B}}^-:\text{C}:::\text{O}^+: & \text{H}:\overset{..}{\text{B}}^-:\text{C}^+::\overset{..}{\text{O}}: \\
\text{H} & \text{H} \\
\text{I} & \text{II} \\
\\
\text{H} & \text{H} \\
\text{H}:\overset{..}{\text{B}}_-::\text{C}::\overset{..}{\text{O}}: & \text{H}:\overset{..}{\text{B}}_-::\text{C}^+:\overset{..}{\underset{..}{\text{O}}}^-: \\
\text{H}^+ & \text{H}^+ \\
\text{III} & \text{IV}
\end{array}
$$
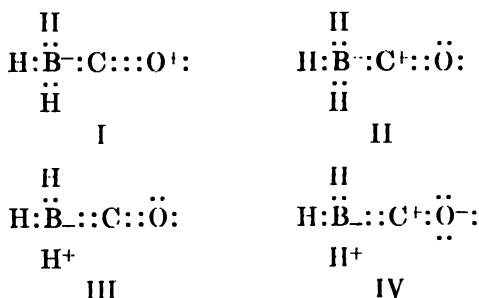
| (There are three of these, and three more involving one-electron bonds between the boron and two of the hydrogen atoms) | (There are three of these, and three more involving one-electron bonds. . .) |

Structures III and IV represent the atomic-orbital formulation of the hyperconjugation effect, and serve to introduce dipole moments opposed to the large ones of I and II.   The extent of the contribution of III and IV cannot be readily estimated; apparently neither in H_3BCO, nor in $(H_3C)_3B$ and $(H_3CBO)_3$, are the effects of sufficient importance to shorten the boron–carbon distance below that expected (8, Tables I and II) for a pure single bond.

E. Trimethylamine-borine, $(CH_3)_3N:BH_3$

The experimental error is large in the case of trimethylamine-borine, owing to the fact that the molecule contains many atoms symmetrically arranged.

Hence no conclusions regarding its electron configuration can be drawn from the observed boron–nitrogen distance. For the ground state only one electron-pair-bond structure need be written:

$$
\begin{array}{ccc}
\text{H} & & \text{CH}_3 \\
\ddot{\text{H}}:\overset{..}{\underset{..}{\text{B}}}{}^{-}:\overset{..}{\text{N}}{}^{+}:\text{CH}_3 \\
\ddot{\text{H}} & & \overset{..}{}\text{CH}_3
\end{array}
$$
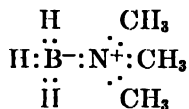
It indicates a fairly high dipole moment, as would be expected from the observed high boiling point of the substance (171°C.).

F. Comparison of borine carbonyl with trimethylamine-borine

Superficially, borine carbonyl and trimethylamine-borine should show similarities in chemical behavior, since the association linkages are analogous from a valence-bond point of view; i.e., the empty fourth orbital of boron is occupied by the unshared electron pair of the nitrogen or carbon. However, an extra-
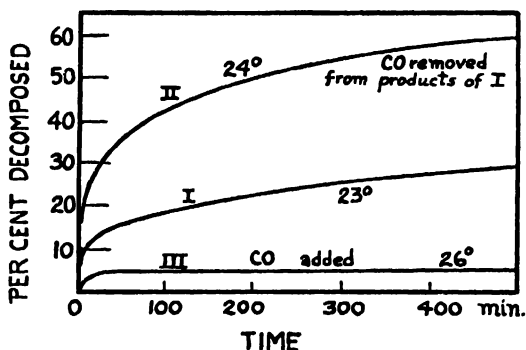
Fig. 4. Rate of decomposition of borine carbonyl (Burg and Schlesinger)

ordinary difference in the stabilities of the two compounds exists (13). Evidently the situation is a complicated one, and it is not certain that strictly similar rôles are played by the unshared electron pairs in carbon monoxide and nitrogen trimethyl. Were this possibility excluded, one might undertake to explain the difference in stability as being due to the fact that nitrogen is twice as far removed from boron on the electronegativity map as is carbon; consequently, the B—N bond may be as much as 17 kilocalories stronger than the B—C bond. (Some deduction, of the order of 3 kilocalories, should be made from this value for the possible double-bond character (hyperconjugation) of the latter linkage.) Since in the *association* of borine with carbon monoxide or trimethylamine no bonds are broken and one covalent bond of the "donor" type is formed per compound, the activation energy is probably the same for these two reactions. But we have argued above that the resultant bond in the carbonyl is weaker to the extent of approximately 14 kilocalories than in trimethylamine-borine; hence the activation energy for the *dissociation* is expected to be smaller for the borine carbonyl by the same amount, leading to the

possibility that the rate constant for $H_3BCO \rightarrow H_3B + CO$ is greater by a factor of 10^{10} than for the analogous reaction for trimethylamine-borine.[5]

From the molecular-orbital point of view there is no formal analogy between the bonds formed in these two association reactions. In the discussion of the structure of carbon monoxide, Mulliken (37, 38) has described the slightly anti-bonding (unshared) pair of electrons as occupying an orbital which is essentially an s-orbital of carbon. On the other hand, in his discussion of ammonia and its methyl derivatives (40), it is principally the $2p_z$-orbital of nitrogen, nonbonding in character, which is occupied by the unshared electron pair. We would accordingly expect a difference in the bonds formed between borine and carbon monoxide or trimethylamine and, indeed, that the latter would form a stronger bond than the former, inasmuch as the bonding power of a p-orbital (with greater concentration of the wave function in the bond direction) is known to be greater than of an s-orbital. The problem is well worth further consideration. The compounds CO_2, H_2CCO, and H_3BCO are isosteric, and would possess similarities in electron configuration, spectra, etc. The first of these has already been discussed by Mulliken (43) and the analogy with borine carbonyl has been indicated.

G. Triborine triamine (borazole), $B_3N_3H_6$

Triborine triamine appears to be analogous to benzene in atomic configuration, interatomic distances, and intramolecular force constants (see below); that there is a correspondence between the electron configurations of the two compounds is therefore strongly indicated. In this respect the analogy is not complete. Whereas in benzene there are three double bonds in every structure which contributes to the ground state, whence the reduction in carbon–carbon distance from the single-bond value of 1.54 Å. to 1.39 Å., in triborine triamine the most important structure is the completely single-bonded one,

$$
\begin{array}{c}
\mathrm{H} \\
| \\
\mathrm{B} \\
\diagup \quad \diagdown \\
\mathrm{H-N:} \qquad \mathrm{:N-H} \\
| \qquad\qquad | \\
\mathrm{H-B} \qquad \mathrm{B-H} \\
\diagdown \quad \diagup \\
\mathrm{N} \\
| \\
\mathrm{H}
\end{array}
$$
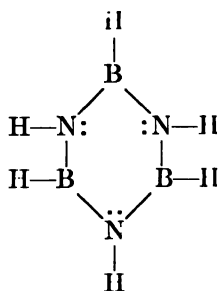
[5] A few preliminary experiments on the kinetics of the dissociation of borine carbonyl have been reported by Burg and Schlesinger (13). At 100°C., the equilibrium constant for the reaction

$$2H_3BCO = 2CO + B_2H_6$$
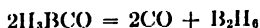
was estimated to be

$$K = \frac{p^2(CO) + p(B_2H_6)}{p(H_3BCO)} \approx 2.9 \times 10^4$$

Owing to the presence of side reactions and other complicating factors, this value is only an approximate one. At room temperature the reaction is very slow; carbon monoxide

while the double-bonded configurations
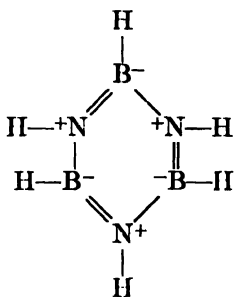
(Two of these and three Dewar structures, etc.)

play a lesser rôle, owing to the fact that the formal charge thus introduced implies an electron distribution which is contrary to the relative electronegativities of the boron and nitrogen atoms. As a consequence, the boron–nitrogen distance is only 0.06 Å. less than that expected for a single bond.

In treating this compound, we should note that the symmetry of the various orbitals used in the discussion of benzene will have to be reduced from sixfold to threefold, and the number of degeneracies, selection rules, etc. changed accordingly.

II. B_2NH_7

The electronic structure of B_2NH_7 cannot be specified until a decision is reached regarding its atomic configuration. If it is $H_2B-NH_2-BH_3$ (54), only one Lewis structure can be written:
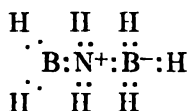
(the formal charges indicate the presence of an appreciable dipole moment), but then it is difficult to account for the observed boron–nitrogen separations (both equal to 1.56 ± 0.03 Å.). From table 2, the single-bond distance should be 1.50 Å. On the other hand, the configuration $H_3B-NH-BH_3$ is much more symmetric and hence would have a smaller moment.[6] The ground state might be represented by a linear combination of a large variety of one-electron and no-bond structures, some of which are shown below.

---

appears to inhibit the attainment of equilibrium, as may be seen from the pressure *versus* time curves of figure 4.

[6] The dipole moment of $NH(BH_2)_2$ would nevertheless be considerably larger than that of $NH(CH_3)_2$, owing to the greater electronegativity difference between nitrogen and boron (one unit) as compared with that between nitrogen and carbon (0.5 unit). The higher boiling point of B_2NH_7 (76.2°C. *versus* 7.2°C.) can therefore be readily explained.

$$H \quad H \quad H$$
$$H : \overset{..}{\underset{..}{B}}{}^{-\frac{1}{4}} . \overset{..}{\underset{..}{N}}{}^{+1} . \overset{..}{\underset{..}{B}}{}^{-\frac{1}{4}} : H \qquad\qquad H_3 \overset{..}{B}{}^{-1} : \overset{..}{\underset{.}{N}}{}^{+1} . \overset{}{B}{}^{-\frac{1}{4}} H_3$$
$$H \qquad H$$

(1)
Type I

(2)
Type II

$$H$$
$$H_3 \overset{..}{B}{}^{-1} : \overset{..}{\underset{..}{N}}{}^{+2} : \overset{}{B}{}^{-1} H_3$$

$$H \quad H \quad H$$
$$H^{+\frac{1}{4}} . \overset{..}{B}{}^{-\frac{1}{4}} : \overset{..}{\underset{..}{N}}{}^{+\frac{1}{4}} . \overset{..}{B}{}^{-\frac{1}{4}} . H$$
$$H \qquad H$$

(1)
Type III

(6)
Type IV

$$H$$
$$H_3 \overset{..}{B}{}^{-1} : \overset{..}{\underset{..}{N}}{}^{+1} BH_3 \quad \text{etc.}$$

(2)
Type V
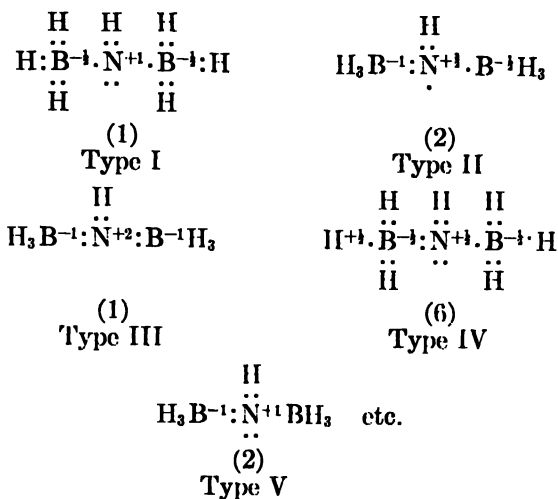
The importance of the contributions made by configurations such as I, IV, and V determines firstly, the extent to which B_2NH_7 possesses the characteristics generally associated with a free electron pair on a nitrogen atom, and secondly, the electron deficiency of the B—N and B—H bonds. The larger than expected boron-nitrogen distances are therefore reasonable. Resonance with types similar to II and III serves to quench the base-like character of the nitrogen atom, as the somewhat similar type of resonance does in pyrrole. A possible, but entirely hypothetical, way of accounting for both the chemical and the physical data is to assume this latter atomic configuration plus a tautomerism, as suggested by Burg.

I. Al(BH₄)₃

The Al—B bonds in Al(BH₄)₃ appear to be single covalent ones of the sp^2 type; the interatomic distance observed is but slightly greater than the sum of the single bond radii (table 2). The boron–hydrogen distances, however, are large, being the same as in B_2H_6, B_4H_{10}, and B_5H_{11}, and this would be expected in view of the six-electron deficiency present in the molecule. Therefore, the ground state could be represented by a linear combination of

$$H_4B \qquad\qquad H \quad H^{+\frac{1}{4}}$$
$$\diagdown$$
$$Al{-}\overset{..}{\underset{..}{B}}{}^{-\frac{1}{4}}$$
$$\diagup$$
$$H_4B \qquad\qquad \overset{..}{H} \quad H^{+\frac{1}{4}}$$
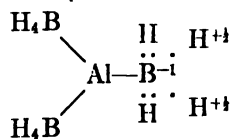
(There are six such configurations per BH₄ group)

in which each BH orbital is occupied by an electron pair half of the time and by one electron the other half, and numerous excited structures, such as

$$H_4B \qquad\qquad H \quad H$$
$$\diagdown$$
$$Al : \overset{..}{B}{}^{-1} \qquad \text{(four per BH}_4\text{ group)}; \quad (BH_4)_2 Al \cdot {-}\overset{..}{B} \quad ; \quad \text{etc.}$$
$$\diagup$$
$$H_4B \qquad H^{+\frac{1}{4}} H \qquad\qquad\qquad\qquad\qquad \overset{}{H} \quad H$$
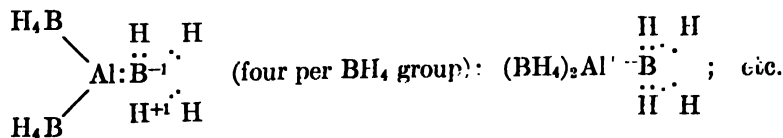
The contribution from ionic structures probably is not appreciable. First, the large boron–hydrogen distances indicate that the electron deficiency resides primarily in the BH_4 groups, and second, the aluminum–boron distances are close to that expected for electron-pair bonding. The extent of such ionic contributions must increase, however, as one goes down the series,

$$Al(BH_4)_3 \qquad Be(BH_4)_2 \qquad LiBH_4$$
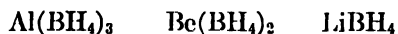
in harmony with the observed decrease in volatility. The electron configuration of the latter compounds could be represented in a fashion similar to that given for $Al(BH_4)_3$. In view of the conclusions reached by Kimball (26) regarding the configurations which could lead to a bipyramidal arrangement of the atoms (dsp^3, d^3sp), it is interesting to note that in these compounds four electrons are as effective as the five needed, provided the molecule permits structures involving one-electron bonds to contribute to the ground state.

TABLE 4

Constants for boron hydride (BH)

	cm. [1]	FORCE CONSTANT megadynes	D_0 volts	r_e Å.
Ground state $A^1\Sigma^+$	$\omega_e = 2366$	0.302	3.60	1.225
Configuration $D^3\Pi$				1.198
Configuration $C^1\Pi$	$\omega_e = 2344$	0.297	0.73	1.219
Configuration $B^3\Sigma^+$				1.220

VII. SPECTROSCOPIC DATA

A. Boron hydride

Fitting in with and extending beyond the structural measurements are conclusions regarding internal symmetry and bond force constants derived from spectroscopic investigations. A number of bands have been observed for boron hydride, BH; these proved the existence of the three excited states enumerated above. The constants of chemical interest deduced from them (27) are shown in table 4.

B. Diborane

The ultraviolet, visible, and infrared spectra of diborane have been mapped. Blum and Herzberg (11) studied the two bands in the ultraviolet which start at about 2200 Å., with no sharp long-wave-length limit, and extend to as short wave lengths as were permitted by the apparatus (1550 Å.). They made the tentative suggestion that the absorption region on the short-wave-length side may be due to a transition from the ground state, the configuration of which is to be roughly approximated by the molecular-orbital description given above (page 49), to one of the many states resulting when a [πe] electron is excited to a [$3sa_1$] orbital; the band with the maximum at 1820 Å. may be produced by a

transition to a somewhat lower state resulting from such an excitation. In both of these upper states, the number of bonding electrons remains the same as in the ground level, and hence both would be stable. However, there would be the tendency for predissociation, which accounts for the continuum observed.

Plumley (49) found no absorption by diborane in the region from 2500 to 12,000 Å.; on the basis of the energy-level diagram given above, the transition $^1A_{1g} \rightarrow {}^1E_u$ (indicated by $\uparrow$ in figure 3) should result in a band at about λ 8000. A tentative explanation of this discrepancy might be that the estimated spread between the ground $^1A_{1g}$ and the excited ^1E_u is approximately five times that actually present. Thus one might expect that the above transition would result in an absorption band between 4 and 5 μ. In his infrared studies of diborane, Stitt (61) found indications that fairly strong bands do occur in that region, and some of these may be electronic in origin. Indeed, it appears that the thermocouple infrared absorption spectrum of diborane has too many bands to permit a simple analysis. Stitt carefully explored the region from 400 to 4000 cm.$^{-1}$ under low dispersion. His tentative conclusions are summarized below.
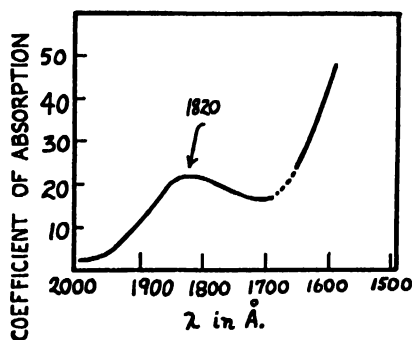
FIG. 5. Absorption of diborane in the ultraviolet (Blum and Herzberg)

The first attack on the problem was undertaken by Anderson and Burg (1), who obtained the Raman spectrum of liquid diborane. They were able to make a preliminary assignment of some of the frequencies and thus obtained an estimate of the stretching and bending force constants through the use of Howard's (23) formulas for the normal modes of vibration of an ethane-like molecule. The results of their assignment are given in table 5. As in the case of ethane and disilane, the constant for the stretching vibration of the bond between the two heavy atoms thus obtained is considerably greater than the one deduced from Badger's rule (2), using the electron-diffraction interatomic distances. Anderson and Burg suggest that in all three cases the apparent compression of the bond, leading to tighter binding, is probably related to the potential hindering freedom of rotation. It should be noted, however, that the discrepancy between the computed and observed distances becomes less, although it is not entirely eliminated, if a potential function including interaction terms is used (59).

Stitt (61) found that a complete analysis of the infrared and Raman spectra of diborane and a satisfactory assignment of all the frequencies observed must

await further work. As in the case of ethane, it is not possible to decide, on the basis of the spectroscopic data alone, whether the molecular symmetry is D_{3h} or D_{3d}. He pointed out that there are two factors which may contribute to the extra complexity of the diborane spectrum: firstly, the occurrence of two abundant isotopes of boron, so that three types of diborane molecules, B^{11}—B^{11}, B^{11}—B^{10}, and B^{10}—B^{10} of the relative concentrations 16:8:1, respectively, must be considered; secondly, the possibility that some of the observed infrared and Raman transitions involve low-lying electronic states.

If the potential function of diborane is not very different from that of ethane, comparison of the spectra of the two molecules emphasizes several striking features: (1) The separation of 421 cm.$^{-1}$ between the two strong Raman lines in the neighborhood of 2300 cm.$^{-1}$ (ν_3, table 5) seems too large to permit their assignment to a resonance degenerate pair; (2) the two very strong infrared

<div align="center">

TABLE 5

Assignment of frequencies to diborane

</div>

		FORCE CONSTANT
B—B stretching (symmetric)		
B^{11}—B^{10} ⎧ 793 cm.$^{-1}$		3.57 × 10^5 dynes per centimeter
B^{11}—B^{10} ν_1........ ⎨ 806		
B^{10}—B^{10} ⎩ 821		
B—H stretching (symmetric)		
ν_3........ ⎧2102 cm.$^{-1}$		3.0 × 10^5 dynes per centimeter. One line expected;
⎩2523		splitting interpreted as a coincidence resonance
		with one of the overtones, as in ethane
B—H bending (symmetric)		
ν_2........ 1180 cm.$^{-1}$		0.26 × 10^5 dyne per centimeter

bands at 1608 and 1863 cm.$^{-1}$ are apparently not assignable to fundamental vibrations; and (3) a strong infrared band appears at 400 cm.$^{-1}$, the origin of which is somewhat perplexing. Stitt found that there are several ways in which these may be accounted for. Accordingly, he presented the following alternate analyses of the main features of the spectrum, both of which are in accord with the heat capacity of gaseous diborane over the temperature interval 100° to 300°K., and both are based on the ethane-like model.

(a) One may assume a singlet low-lying electronic state at 412 cm.$^{-1}$ and another at 1863 cm.$^{-1}$, to which transitions from the ground state are permitted. The strong absorption region at 1608 cm.$^{-1}$ would then be due to an electronic-vibrational transition (a combination of the 412 cm.$^{-1}$ and one of the parallel deformation frequencies), as would also the Raman line at 2102 cm.$^{-1}$ A potential barrier of approximately 15 kilocalories hindering free rotation about the B—B bond (corresponding to a torsional frequency of 605 cm.$^{-1}$) must be assumed in order that the heat-capacity data may be accounted for. The band

at 1863 cm.$^{-1}$ has two peaks and hence, if due to an electronic transition, may be one of the components of the complex of bands resulting from the transition $^1A_{1g} \rightarrow {}^1E_u$. In Mulliken's energy-level diagram there appears no allowed transition from the ground level which could give rise to the band at 412 cm. ^{1}, even if one assumes that his scale is considerably overextended. Also, the very large potential barrier hindering internal rotation is difficult to accept for an ethane-like model, particularly when the observed boron-boron distance is considerably greater than expected for a single bond.

(b) One may assume that the bands at 1608 cm. ^{1} and 1863 cm.$^{-1}$ are due to electronic transitions from the ground state to two low-lying levels; the 412 cm.$^{-1}$ absorption is assumed to be an electronic-vibration difference band and the Raman line at 2102 cm.$^{-1}$ is assigned as above. Then the more reasonable restricting potential of 5 kilocalories (corresponding to a tortional frequency of 350 cm.$^{-1}$) is satisfactory for the interpretation of the specific-heat data. (In computing the heat capacities for both (a) and (b), the electronic state at 1608 cm.$^{-1}$ was assumed to be triply degenerate.) A difficulty remains, however, since the band at 1608 cm. ^{1} is the strongest one of the infrared bands observed for diborane, and appears to be of the *parallel* type. Assuming that the symmetry D_{3d} (hydrogen atoms staggered) is retained during transitions from the ground state, one might expect (42)

$$^1A_{1g} \rightarrow {}^3E_u, {}^3A_{2u}, {}^3E_u, {}^1E_u$$

of which the singlet-triplet transitions are known to be weak for molecules as light as diborane, while the $^1A_{1g} \rightarrow {}^1E_u$ should be the most intense, resulting in a *perpendicular*-type band, as indeed the one at 1863 cm.$^{-1}$ appears to be. Of course, it is quite possible that the *excited* states have a lower symmetry than D_{3d} (for instance, the splitting of the ^1E_u state into two non-degenerate singlet ones, according to the Jahn-Teller theorem), so that the estimated relative intensities based on the above selection rules may be quite inaccurate.

R. S. Mulliken has suggested two other possible causes for the complexity of the diborane spectrum. Firstly, owing to the probable changes in the equilibrium positions of the atoms during the electronic transition, vibrational excitation in the upper state should be considered (Franck–Condon principle). Hence $^1A_{1g} \rightarrow {}^1E$ may result in several strong electronic-vibrational bands. Secondly (and much less probably), there still exists the possibility that the *ground* state does not have the symmetry D_{3d}, as it may be one of the components of the split ^1E state. The discussion of the electron configuration of diborane, selection rules, etc. given above would then have to be revised.

No extensive normal coördinate treatment such as was carried through by Stitt for ethane (59) was undertaken for diborane, since the frequency assignment is considerably in doubt.

C. Triborine triamine (borazole)

Triborine triamine has been carefully studied as to both infrared and Raman spectra by Crawford and Edsall (16). The data are best interpreted by assuming

the symmetry D_{3h}, as given by the electron-diffraction measurements. The normal modes of vibration were obtained in a manner similar to that proposed for benzene by Wilson (71), and the observed frequencies assigned. Throughout, the similarity to the latter molecule is rather striking. Indeed, Crawford and Edsall found discrepancies between the calculated (from Raman spectra) and observed (infrared) frequencies of the non-planar bending B—H and N—H modes in triborine triamine, corresponding to the similar discrepancy observed for the non-planar bending C—H frequency in benzene. For comparison, they tabulated the various force constants (see table 6) for the two molecules; the approximate characters of the corresponding vibrations are indicated. Note the general correspondence between the B—H stretching and bending frequencies in triborine triamine and in benzene.

TABLE 6

Force constants for triborine triamine and for benzene

$B_3N_3H_6$		C_6H_6	
Planar:		*Planar:*	
K	(B—N stretching).......6.300 × 10⁵ dynes per cm.	K	(C—C stretching)......7.58 × 10⁵ dynes per cm.
k	(B—N—B or N—B—N bending)..............0.525	k	(C—C—C bending).....0.65
H_B	(B—H bending).........0.35	H	(C—H bending)...... 0.76
H_N	(N—H bending).........0.65		
q_B	(B—H stretching).......3.423 $\nu = 2535$	q	(C—H stretching)......5.05
q_N	(N—H stretching).......6.524 $\nu = 3450$		
Non-planar:		*Non-planar:*	
κ	(B—N torsion)........0.10	κ	(C—C torsion) 0.23
h_B	(B—H bending).........0.23	h	(H—CH bending).....0.34
h_N	(N—H bending).........0.42		

Crawford and Edsall found four intense Raman lines with the shifts 851, 938, 2535, and 3450 cm.⁻¹; these were the only lines found to be polarized. They were therefore assigned to the non-degenerate symmetric class (A'_1). The last two frequencies are readily identified with the B—H and N—H stretching, respectively.

VIII. THERMODYNAMIC FUNCTIONS FROM SPECTRAL AND STRUCTURAL DATA

Upon combining the spectroscopic and diffraction data, a number of thermodynamic functions may be computed. This has been done for diborane (1) and for triborine triamine (16). Anderson and Burg assumed an entropy contribution due to internal "torsional" vibration of 2.4 E.U., and obtained, for the entropy of the ideal gas at 25°C., $S^*_{298} = 55.3 \pm 1.5$ calories per mole per degree and for the entropy of formation, $\Delta S^0_{298} = -50.4 \pm 3.5$ calories per mole per

degree. The assumption regarding the torsional vibration is now justified by the specific-heat data on diborane (60). Such a vibration would contribute 2.0 E.U. to the entropy, while for completely free rotation the contribution is 3.3 E.U. Further, by combining the experimentally determined heat of formation of diborane (51, 52) (44 ± 3 kilocalories) with their computed entropy, Anderson and Burg were able to estimate the free energy of formation of diborane (from the elements): $\Delta F^0_{298} = -30 \pm 4$ kilocalories. In this computation they had to assume that the entropy of solid boron is 4 ± 1 calories per mole per degree at 298°K.

The results of statistical computations made for triborine triamine (16) are given in table 7. Values in calories per mole per degree are tabulated for various temperatures for the perfect gas at 1 atm.

TABLE 7

Results of statistical computations made for triborine triamine

T	S°	$-(F^0 - E_0^0)/T$	c_p^0
°K.			
298.1	73.7	60.4	23.3
326†	75.8	61.5	25.3
350	77.7	62.6	27.1
400	81.5	64.8	30.4
500	88.9	68.7	36.0
600	95.9	72.6	40.5
700	102.5	76.6	44.2
800	108.5	80.2	47.2
900	114.2	83.6	49.6
1000	119 6	87.0	51.8

From vapor pressure data, and these values:

$S^0_{298}(l) = 51.0$

$S^0_{326}(l) = 53.4$ (boiling point)

$[(F^0 - E_0^0)/T]_{298}(l) = 62.5$ calories per mole-degree

† Boiling point.

IX. THERMOCHEMICAL MEASUREMENTS AND SPECIFIC HEAT OF DIBORANE

The heats of vaporization and sublimation of many of the hydrides and of their derivatives have been obtained from their vapor-pressure curves. The heats of formation of several boron compounds have been deduced indirectly. Thus Kelley (25) gives

for B(s): $C_p = 1.54 + 4.40 \times 10^{-3}T$ for $T < 1,173°$

and

for BN(s): $C_p = 3.22 + 8.00 \times 10^{-3}T$ for $T < 1,173°$

Then, from equilibria measurements on the thermal decomposition of boron nitride, he computed for the reaction BN = B + ½N₂,

$$\Delta H_{298} = 31.5 \text{ kilocalories}$$

$$\Delta F_{298} = 27.7 \text{ kilocalories}$$

The work of Roth and Börger (51) and of Roth, Börger, and Bertram (52) appears to be the only direct calorimetric measurements on the compounds of boron. Their final results may be summarized by the following equations:

$$2B(s) + 1.5O_2(g) = B_2O_3(s) + 349 \pm 2 \text{ kilocalories}$$

$$B_2H_6(g) + 3H_2O(l) = B_2O_3(s) + 6H_2(g) + 100.2 \pm 2.1 \text{ kilocalories}$$

$$2B(s) + 3H_2(g) = B_2H_6(g) + 44 \pm 3 \text{ kilocalories}$$
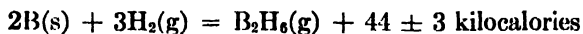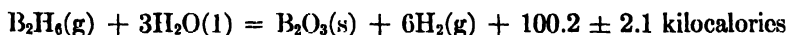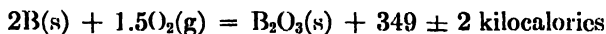
These investigators call attention to the fact that the heat of formation of ethane (20.96 kilocalories) is about half that of diborane.
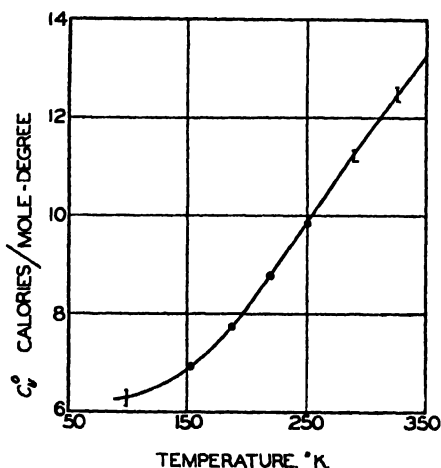
FIG. 6. The gaseous heat capacity of diborane, as a function of the temperature (Stitt)

Stitt measured the heat capacity of gaseous diborane over the temperature range 95° to 324°K. (60) by means of the low-pressure thermal conductivity apparatus first used for ethane (28). His results are presented graphically in figure 6. The heat capacity (C_v) at the lowest temperature is particularly interesting, since the translational and over-all rotational contribution is $3R = 5.96$ calories per mole, while the observed value is 6.35 ± 0.2 calories per mole. The small difference 0.4 ± 0.2 calorie per mole is all that is left for the internal rotational degree of freedom. This indicates an appreciable barrier restricting rotation about the B—B bond; indeed, Stitt computed a height between 3300 and 6000 calories per mole, assuming that the barrier is of a cosine form. From the heat capacity at 142°K., he deduced that the lower limit is 4 kilocalories per mole. On the other hand, the estimate of the upper limit is valid provided the vibrational and electronic contributions to the specific heat at 100–150°K. are negligible. The barrier will be considerably higher if a very low lying electronic state is postulated, as was discussed above. Whichever assignment is selected

[(a) → 15 kilocalories; (b) → 5 kilocalories], the specific-heat curve may be reproduced accurately over the entire range. For comparison, the barrier in ethane is considered to be of the order of 3 kilocalories per mole.

X. DIELECTRIC POLARIZATIONS

Ramaswamy (50) made dielectric-constant measurements on the vapors of two of the hydrides. The dipole moments deduced for diborane and triborine triamine from his data are zero and 0.67 D, respectively. The first value is that which would be predicted both by the Sidgwick–Lewis and the Mulliken electron configurations; in both schemes the over-all symmetry of diborane is D_{3d}, owing to the linear combination of the individual structures contributing to the ground state. The small but non-vanishing moment for triborine triamine is in disagreement with both the diffraction and the spectroscopic data, which assign to the molecule the symmetry D_{3h}. However, Ramaswamy admits that the data on the latter compound are doubtful, as the presence of impurities in the sample used was later established.

TABLE 8

Values for the molecular polarizations of some compounds

COMPOUND	P_T	P_E	P_A
C_2H_6	11.16	11.07	0.09
B_2H_6	14.46	12.91	1.55
Si_2H_6	28.10	23.72	4.38
C_6H_6	27.01		
$B_3N_3H_6$	23.76 (?)	20.18 (?)	3.58 (?)

Values for the molecular polarizations of the two hydrides are given in table 8. For comparison, data on several analogous compounds are included (69).

XI. MAGNETIC SUSCEPTIBILITIES

Since paramagnetic molecules or ions were found to catalyze the conversion of para- to ortho-hydrogen, Farkas and Sachsse (19) tested diborane for paramagnetism by studying its effectiveness in the conversion. They obtained no reaction at 195°K. and concluded that the ground state is diamagnetic. They set a lower limit for the first paramagnetic level at 3000 calories above the lowest energy state, and suggested that it is undoubtedly higher. To explain the small amount of conversion which was obtained at 293° and 373°K., they postulated the *exchange* reaction

$$H_2(p) + B_2H_6 = B_2H_6 + H_2(o)$$
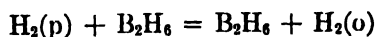
and estimated the heat of activation to be about 15 kilocalories. Freed and Thode (20) measured directly the diamagnetic susceptibility of diborane (Gouy method); they found no evidence for the presence of a low-lying paramagnetic state ($^3A_{2g}$) at room temperature.

$$\chi_{B_2H_6} = -17 \times 10^{-6} \text{ per mole}$$

For comparison, $\chi_{C_2H_6} = -30 \times 10^{-6}$, and the value expected for $B_2H_6^{--}$ from the atomic susceptibilities (30, 66) is

$$\chi_{B_2H_6}{}^{--} = -31 \times 10^{-6}$$

In contrasting the value for diborane with that of ethane, one would conclude that of the two opposing factors, one which tends to give a larger χ, owing to the greater interatomic distances ($\overline{r^2}$ larger), and the other which serves to decrease χ, owing to a lower electron density (twelve instead of fourteen electrons, spread over a larger volume), the latter seems to predominate. At any rate it is clear from these measurements that the ground state of diborane is singlet.

The magnetic susceptibilities of two of the potassium salts were determined by Klemm and Klemm (29); both were found to be diamagnetic (see table 9). The data prove that $K_2B_2H_6$ and $K_2B_2O_2H_6$ are the correct formulas, whereas KBH_3 and $K(OBH_3)$, respectively, (these would be paramagnetic) are incorrect. The slight paramagnetic contribution which appears in $K_2B_2H_6$ as the tempera-

TABLE 9

Magnetic susceptibilities of $K_2B_2H_6$ and $K_2B_2O_2H_6$

T	$\chi_{(gm)}$ $K_2B_2H_6$	$\chi_{(gm)}$ $K_2B_2O_2H_6$
°K.		
90	-0.60×10^{-6}	
195	-0.57	
293	-0.42	-0.5 to -0.3×10^{-6}
353	-0.34	

ture is raised has no clear explanation. The magnetic behavior of $B_2H_6^{--}$ should parallel that of ethane. The lowest excited state of the latter compound results from the excitation of one of the C—C bonding electrons (41); i.e., ethane assumes the configuration $[\sigma + \sigma, a_1]^{-1}(3sa_1)$, ${}^3A_1$, ${}^1A_1$. The position of the paramagnetic level is unknown, owing to the fact that transitions from the ground state to it are forbidden. Because of the lower nuclear charge, the ${}^3A_1$ state in $B_2H_6^{--}$ should be considerably below that of ethane. Assuming that the observed paramagnetic effect was not due to an impurity,[7] the position of that level was estimated to be about $6.2\ kT$ (at $T = 300°C$.) above the ground state, much lower than would have been expected.

XII. SURFACE-TENSION DATA

Stock, Wiberg, and Mathing (64) measured the (liquid–vapor) interfacial tension of diborane at various temperatures. Over the temperature range $-110°$ to $-90°C$., the equation for the density of the liquid is

[7] The diamagnetic susceptibility expected for $K_2B_2H_6$ is -58.1×10^{-6} per mole (30, 66), somewhat less than the value observed at the lowest temperature (-63.5×10^{-6} per mole). This might be used to argue against the possible presence of a paramagnetic impurity in the sample.

$$D = 0.4371 + 1.0115 \times 10^{-3}(180.6 - t)$$

Values for the surface tension are given in table 10 and plotted in figure 7. The mean value for the parachor deduced through the equation

$$P = \frac{M}{D_1 - D_v} \gamma^{1/4}$$

TABLE 10

Surface-tension data for diborane

T	γ	T	γ	T	γ
°C.		°C.		°C.	
−119.0	17.16	−112.3	16.30	−102.8	11.84
−118.6	17.26	−111.8	16.36	−91.8	13.78
−117.2	16.98	−108.3	15.82	−94.5	13.70
−116.0	16.88	−108.1	15.67	−92.1	14.11
		−105.9	15.18		

$$\text{Slope } \frac{\partial \gamma}{\partial T} = -0.146$$
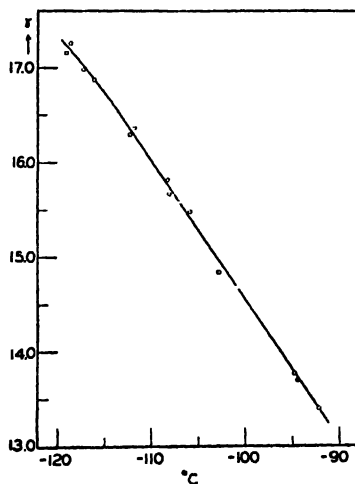
FIG. 7. The surface tension of diborane (Stock *et al.*)

is reported by them to be 121.9. This measurement was recently confirmed by Laubengayer and coworkers (31). By making some rather arbitrary assignments for the contribution of the H^+ (a value of zero) and the one-electron bonds, Stock, Wiberg, and Mathing sought to prove that the parachor computed on the basis of Wiberg's structure of diborane was in agreement with the one obtained experimentally, whereas the ones computed for other structures were in definite disagreement. These conclusions are highly questionable (3, 31). Data on the surface tensions of the other hydrides are not yet available.

XIII. IONIZATION BY ELECTRON IMPACT

Very recently J. A. Hipple has studied the ionization and dissociation of diborane through electron impact by means of a mass spectrograph (22). Relative intensities of the ions observed (90 volt electrons) are given in table 11, and are compared with the relative intensities of the corresponding ions formed in ethane, under comparable conditions. It is particularly interesting to note that (a) $B_2H_6^+$ does not appear; presumably, an electron deficiency of three makes the ion unstable. (b) BH_3^+ and BH_2^+ and BH^+ do not appear, whereas the $B_2H_n^+$ ions are prominent. Since the dissociation process takes place at low pressures, the ions formed are primary collision products. Hence the prominence of B_2H^+ and the definite presence of B_2^+ appear to be strong evidence against the bridge structure. Dr. Hipple is continuing with his very interesting investigations, and is planning to determine the appearance potentials of the above ions. Eventually, an analysis similar to the one that he made for ethane may be possible (21).

TABLE 11

Relative intensities of ions formed by electron impact

ION	RELATIVE INTENSITIES		ION	RELATIVE INTENSITIES		ION	RELATIVE INTENSITIES	
	Boron	Carbon		Boron	Carbon		Boron	Carbon
$X_2H_6^+$	0	100	$X_2H_2^+$	63.7	62	XH_3^+		9
$X_2H_5^+$	100	76	X_2H^+	29	12	XH_2^+		6
$X_2H_4^+$	44.8	360	X_2^+	2.2	2.5	XH^+		2.5
$X_2H_3^+$	21.7	105	X^+	40	1	H^+		50
$X_2H_6^{++}$		1				H_2^+		5
$X_2H_3^{++}$		0.1				H_3^+		0.5

XIV. CONCLUSIONS

Boron was found to be either tri-, tetra-, or penta-coördinated in the compounds the structures of which have been determined. The interatomic distances observed can be readily interpreted in terms of resonance among several Lewis structures, provided R_B is assigned a value close to 0.85 Å., and the formula proposed by Schomaker and Stevenson (56), in which the electronegativity difference between the bonded atoms is considered, is employed. The observed boron–hydrogen and boron–boron separations in B_2H_6, B_4H_{10}, B_5H_{11}, B_5H_9, and $Al(BH_4)_3$ are considerably larger than those predicted in this manner. A resonating system of structures involving one-electron bonds and no bonds, as well as electron-pair bonds, is therefore postulated.

The apparent lack of a fixed coördination number for boron suggests that several opposing factors of comparable importance are to be considered; the observed behavior is the result of a balance between various tendencies, summarized by the following set of empirical statements:

(a) 5.35 electron volts are required to promote the configuration of boron

from the ground state (s^2p, ^2P) to that required for the formation of three planar bonds (sp^2, ^2D). This excitational energy must be less, but not much less, than the stabilizing energy due to bond formation. The boron trialkyls are the only known examples of this case. The tendency of these compounds to associate with other molecules indicates that type (d) below is a more stable coördination.

(b) In all other stable compounds boron assumes a formal charge, varying in value from 0 to -1, in order that it may participate in the sharing of more than three electron-pair bonds. The electron affinity of boron is very little (estimated at a tenth of a volt), but the promotional energy for B [1] (s^2p^2, $^3P \rightarrow sp^3$, ^5S) is probably also low (in the order of 4.7 volts); stabilization due to an increase in the number of bonds may therefore take place. Three types of bindings may result.

(c) In the first of these, boron remains tricoördinated, but at times shares an extra electron pair belonging alternately to one of its neighbors (chlorine, oxygen, and nitrogen are examples). A resonating system like that present either in graphite or in benzene results. Generally, this separation of formal charge ($> B^- = {}^+X$) is opposed by the relative electronegativities of the atoms, so that such contributions are not extensive.

(d) In the second group, boron is tetracoördinated, and either shares an electron pair of the donor type, thus assuming a formal charge of -1 (H_3BCO, $(C_2H_5)_2O:BF_3$, and $H_3N:B(CH_3)_3$ are examples), or where there is an insufficiency of electrons to give the boron a full formal charge of -1, a resonating system of the type present in diborane results, provided the boron atom is attached to hydrogen or to other boron atoms, for which linkages one-electron bonds are permissible (presumably owing to the fact that the electronegativities of boron and hydrogen are almost equal).

(e) In the last group boron is pentacoördinated. It appears quite reasonable that a formal charge greater than -1 requires more excitational energy than could be counterbalanced by the stabilizing effect of the five bonds; hence, pentacoördinated boron occurs only when most of its bonds are to hydrogen or other boron atoms, for which linkages one-electron bonds are possible. A resonating system involving electron-pair-bond, one-electron-bond, and no-bond structures results in a set of directed valences such as would be due to dsp^3 or d^2sp^2 (Al(BH$_4$)$_3$ or CaB$_6$, respectively) or equivalent configurations with a formal charge of only -1 on the central boron atom.

(f) Where there is an electron deficiency, it is always even; if odd, the ground state would be at least doublet, and there would probably be several low-lying excited states, a condition usually associated with high energy or particular reactivity in the case of polyatomic molecules. Favorable circumstances are required for the deficiency to be greater than four; a deficiency of six present in Al(BH$_4$)$_3$ appears to be the largest found to date; CaB$_6$ may have a deficiency of ten per B$_6$ group, but such an assignment is arbitrary and depends on how the electrons are distributed in the crystal.

The spectra of the hydrides of boron and derivatives which have been studied show strong similarities to those of the corresponding carbon compounds. In

general, the observed physical and chemical properties are in agreement with the assigned electron configurations.

I wish to thank Professors Mulliken, Schlesinger, and Burg for their interest in this paper. They read the manuscript prior to publication and offered several helpful suggestions.

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THE ADDITION OF HYDROGEN TO MULTIPLE CARBON–CARBON BONDS

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CONTENTS

I. INTRODUCTION

The methods used for the reduction of multiple carbon–carbon bonds may be divided into three large groups: chemical, electrolytic, and catalytic. Since the nature and location of the unsaturation determine to a large extent the course of the reduction, the discussion of each class of reducing agent has been further subdivided according to the type of compound studied.

The object of this review has been to collect and correlate the data available on the use of the three methods, and to show the usefulness and limitations of each method. An especial effort has been made to include a complete survey of chemical and electrolytic methods; since, however, there are many excellent reviews on catalytic hydrogenation, only those references which seemed most pertinent have been included.[1]

II. CHEMICAL REDUCTION

A. Introduction

The reducing agents in the chemical group include all the dissolving metal combinations, such as sodium in alcohol, sodium amalgam, sodium in liquid ammonia, zinc and tin in neutral, acid, or basic media, zinc amalgam, aluminum amalgam, etc., as well as the soluble metal salts which are reducing agents, such as vanadous, chromous, and titanous chlorides. As a matter of fact, however, most of the work has been done with the alkali metals and with aluminum amalgam.

The chemical reduction of multiple carbon–carbon bonds has been studied, in the course of the last half-century, by a large number of investigators. Out of the welter of results, which are not always concordant, a few definite generalizations emerge. Simple, purely aliphatic olefins, such as amylene (184), are not reduced by dissolving metals or other chemical reducing agents. The presence of an aryl, carbonyl, or ethylene group conjugated with (or in some cases cumulated with) the unsaturation is essential for reduction to occur, although the presence of such conjugation does not make it certain that reduction will take place with all of the reducing agents included in this group. This necessity of conjugation for the chemical reduction of an ethylenic group to occur is in sharp contrast to the results of catalytic hydrogenation, where the simple ethylene bond is reduced more easily than the conjugated one.

Simple acetylenes, unlike olefins, are reduced by some chemical reducing agents, especially by sodium in liquid ammonia, and since the olefins obtained are not further attacked under these conditions, this reaction is a useful one for the preparation of pure olefins (56). Simple aromatic hydrocarbons of the benzene series are in general not reducible by the agents considered in this group, but polynuclear hydrocarbons are.

B. Theories of chemical reduction

Any mechanism proposed to explain the chemical reduction of unsaturated carbon–carbon linkages must satisfy several conditions. It must account for the dimolecular products sometimes encountered, for the mixture of 1,4- and 1,2-dihydro products obtained from conjugated dienes, for the *trans* reduction of acetylenes, and, of course, for the influence of activating groups. Several theories, fulfilling most of these requirements, have been proposed; they differ chiefly in attributing the reduction to the addition of 'nascent' hydrogen atoms (or sodium atoms) or to the addition of electrons and positive ions.

[1] The literature has been surveyed in Chemical Abstracts to January 1, 1942.

The oldest theory proposed to explain the chemical reduction of carbon–carbon unsaturation is that of Bacyer (23), who considered that the dissolving metal reacted with the solvent to liberate hydrogen atoms, and that these 'nascent' hydrogen atoms then reacted with the organic compound before they could combine with each other to form molecular hydrogen. The solvent, according to this theory, would have a direct rôle in the reaction. This theory receives some support from an observation of Wooster (336, 338), who found that toluene was not attacked by sodium in liquid ammonia unless water was present but that then reduction occurred.

Until recent years the theory of 'nascent' hydrogen was widely accepted, and is still used by many authors. Willstätter and his coworkers (328) have, however, rejected this 'nascent'-hydrogen mechanism, as the result of a careful study of the course of reductions by sodium amalgam. They showed that it was possible to obtain yields of reduced product as high as 90 per cent (based on sodium), and considered that this would be impossible if hydrogen atoms were the actual reducing agent. They also showed that the ability of sodium amalgam to react with water with the liberation of hydrogen, and its activity in reducing double bonds, are not parallel properties; it is possible to prepare a sodium amalgam which does not react appreciably with water, and yet shows a high degree of efficiency in reducing a compound such as terephthalic acid. These facts led Willstätter to propose that sodium amalgam reductions occur by the addition of metallic sodium to the double bond, followed by hydrolysis due to the solvent. In this case the solvent takes no direct part in the fundamental reaction.

$$C_6H_5CH{=}CHC_6H_5 + 2Na \rightarrow C_6H_5\underset{\overset{|}{Na}}{C}H{-}\underset{\overset{|}{Na}}{C}HC_6H_5 \xrightarrow{H_2O} C_6H_5CH_2CH_2C_6H_5$$
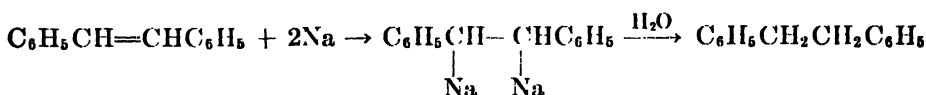
If it is postulated further that the two sodium atoms add, not simultaneously but consecutively, it is possible, by this mechanism, to account for the dimolecular, pinacol-like products that are frequently obtained, especially in the reduction of unsaturated ketones by alkali metals, and for the mixture of 1,2- and 1,4-dihydro products formed in the reduction of diene acids by sodium amalgam.

$$2C_6H_5CH{=}CH{-}\underset{\overset{\|}{O}}{C}{-}C_6H_5 + 2Na \dashrightarrow 2C_6H_5\overset{\bullet}{C}H{-}CH{=}\underset{\overset{|}{ONa}}{C}{\cdot}C_6H_5$$

$$\underset{\underset{ONa}{|}}{\overset{\overset{ONa}{|}}{\underset{C_6H_5CH{-}CH{=}C{-}C_6H_5}{C_6H_5CH{-}CH{=}C{-}C_6H_5}}} \xrightarrow{H_2O} \underset{C_6H_5CH{-}CH_2{-}\underset{\overset{\|}{O}}{C}{-}C_6H_5}{\overset{\overset{O}{\|}}{C_6H_5CH{-}CH_2{-}C{-}C_6H_5}}$$
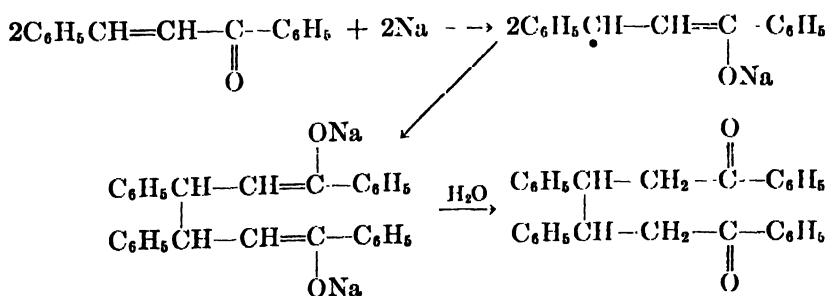
Willstätter's theory has received considerable support from the studies that have been made in the last two decades on the addition of alkali metals to olefins in inert media. In general it is true that those olefins such as cyclohexene, which

can not add sodium or other alkali metals, can not be reduced by dissolving metal combinations, while those that readily add sodium, such as styrene, stilbene, tetraphenylethylene, etc., are reducible by dissolving metals. Furthermore, Wooster and Smith (340) have shown that alkali-organic compounds are intermediates in the reduction of many substances, such as naphthalene, by sodium in liquid ammonia.

Kuhn and Hoffer (175) have proposed a theory very similar to Willstätter's, to explain the reduction of diene acids by dissolving metals. They consider that the reaction consists in the stepwise addition of sodium atoms (or hydrogen atoms) to the unsaturated group, the first addition being to the carbon atom adjacent to the most negative substituent. The monosodium or monohydro compound thus formed can add a second atom, or it can tautomerize and then complete the addition. The relative amounts of the two products will depend on the relative stabilities of the two intermediate radicals:

$$CH_3CH{=}CH{-}\underset{\underset{C_6H_5}{|}}{C}{=}CHCOOH \xrightarrow{[H]}$$

$$CH_3CH{=}CH{-}\underset{\underset{C_6H_5}{|}}{\overset{\bullet}{C}}{-}CH_2COOH \xrightarrow{[H]} CH_3CH{=}CH{-}\underset{\underset{C_6H_5}{|}}{CH}CH_2COOH$$

$$CH_3\overset{\bullet}{C}H{-}CH{=}\underset{\underset{C_6H_5}{|}}{C}{-}CH_2COOH \xrightarrow{[H]} CH_3CH_2CH{=}\underset{\underset{C_6H_5}{|}}{C}{-}CH_2COOH$$

Against Willstätter's theory as a general explanation, several objections have been raised. Hückel (130) has pointed out that it is reasonable to assume that the mechanism of reduction by dissolving metals is the same for all the metals used— sodium, aluminum, zinc, calcium, etc.—and that it seems unlikely that a polyvalent atom such as calcium could add to the 1,4-positions of naphthalene, for example, yet naphthalene is reduced to the 1,4-dihydro derivative by both sodium and calcium in liquid ammonia. Hückel has further emphasized the fact that organo-alkali compounds, such as disodium naphthalene and calcium naphthalene, do not have a covalent bond between the metal and the carbon atom, but are in reality salts; hence in the formation of these substances from the metal and the hydrocarbon, only electrons need to be transferred from the former to the latter. Wilson (332) and Isaacs and Wilson (143, 144, 145) have shown that the electrolytic reduction of conjugated acids such as sorbic acid by high-overvoltage electrodes (mercury, lead) seems to take the same course as does reduction by sodium and sodium amalgam, and may well proceed by the same mechanism, in which case, of course, it cannot involve addition of metal atoms to the double bond.

Several investigators have proposed an ionic mechanism to account for reduction by chemical reducing agents. Conant and his students (63, 65) sug-

gested that the reduction of maleic acid by soluble reducing salts consists of the stepwise addition of two electrons and two hydrogen ions to the oxygen atoms at the ends of the conjugated chain, followed by irreversible ketonization.

$$
\begin{array}{ccc}
\overset{\displaystyle OH}{\underset{\|}{CH}}\!\!-\!\!\overset{\diagup}{C}\!\!=\!\!O & & \overset{\displaystyle OH}{\underset{|}{CH}}\!\!=\!\!\overset{\diagup}{C}\!\!-\!\!OH & & \overset{\displaystyle OH}{\underset{|}{CH_2}}\overset{\diagup}{C}\!\!=\!\!O \\
\overset{\displaystyle}{CH}\!\!-\!\!\overset{}{C}\!\!=\!\!O & +\ 2e\ +\ 2H^+ \longrightarrow & \overset{}{CH}\!\!=\!\!\overset{}{C}\!\!-\!\!OH & \longrightarrow & \overset{}{CH_2}\overset{}{C}\!\!=\!\!O \\
\diagdown OH & & \diagdown OH & & \diagdown OH \\
\text{Maleic acid} & & & & \text{Succinic acid}
\end{array}
$$

Similar theories have been proposed by Michaelis and Schubert (211), who considered that reduction consisted in the consecutive addition of two electrons, followed by two protons, and by Prins (243, 244), who suggested that a proton-electron complex first added to the unsaturated linkage, and that this step was followed either by dimerization, or by the addition of a second proton-electron complex.

The ionic theory put forward by Burton and Ingold (54) can be elaborated to cover practically all types of reduction by chemical reducing agents. In brief this theory is as follows: The double bond polarizes in the reaction medium. For this to occur, at least one carbon atom of the double bond must be attached to a strongly electron-attracting group (aryl, carbonyl), so that one carbon atom of the double bond can provide a seat for the negative charge. The 'polarized' molecule then adds a proton from the solution, forming a positive fragment,[2] which can stabilize itself by acquiring two electrons from the metal surface (or reducing salt), followed by another proton. If the fragment acquires but one electron instead of two, a free radical will be formed which can stabilize itself by dimerization. It will be seen that this theory can be adapted to explain the mixture of 1,4- and 1,2-dihydro products sometimes obtained from conjugated compounds, for the intermediate positive fragment can undergo an allylic rearrangement to a tautomeric form. If it is assumed that a sodium ion can be added in place of a proton when the reduction is carried out by sodium in liquid ammonia, then this mechanism will also explain the formation of disodium naphthalene as an intermediate in the reduction of naphthalene under these conditions.

$$
\begin{array}{ccccccc}
\overset{H\ \ H}{RC::CR'} \rightarrow & \overset{H\ H}{\underset{\cdot\cdot}{RC:CR'}} & \underset{\rightleftharpoons}{\overset{H^+}{}} & \overset{H\ H}{\underset{H\ \ *}{RC:CR'}} & \overset{1e}{\longrightarrow} & \overset{H\ H}{\underset{H\ \ \bullet}{RC:CR'}} & \longrightarrow & \overset{H\ \ H}{\underset{\underset{H\ \ H}{RCH:CR'}}{RCH:CR'}}
\end{array}
$$

$$\downarrow 2e$$

$$
\overset{H\ H}{\underset{H\ H}{RC:CR'}} \xleftarrow{H^+} \overset{H\ H}{\underset{H\ \ \cdot\cdot}{RC:CR'}}
$$
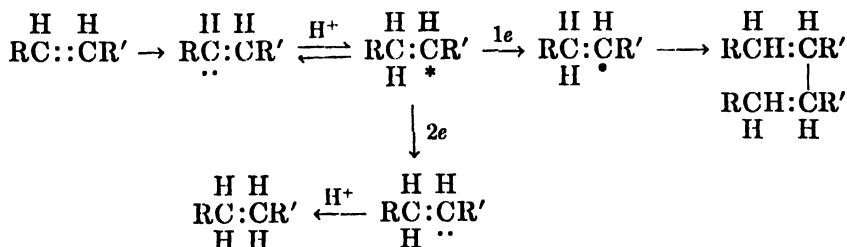
[2] The asterisk designates a carbon atom with only six electrons in the outer shell.

C. Reduction of olefins

Simple aliphatic olefins are not reduced by alkali metals in alcohol or liquid ammonia; neither do they add these metals in inert media. Lebeau and Picon (184) could obtain no evidence of reduction of pinene, cyclohexene, terpinene, etc., when these hydrocarbons were treated with sodium in liquid ammonia. The presence of an aryl, carbonyl, or second ethylene group conjugated to the double bond is essential for reduction to occur.

The presence of one aryl group adjacent to an ethylenic bond activates it sufficiently to permit reduction by alkali metals in many cases. These reductions may be carried out by three more or less general methods: (a) The olefin may be treated with an alkali metal in an inert medium such as ether, followed by hydrolysis of the organo-alkali compound. (b) A solution of sodium in liquid ammonia may be used, followed by hydrolysis. (c) Sodium or sodium amalgam may be used in alcoholic or aqueous media. These methods do not always give the same results with a given olefin. Of the three, sodium in liquid ammonia would appear to be the strongest reducing agent, and sodium amalgam the weakest.

In connection with method (a)—the addition of alkali metals to arylolefins in inert media —the work of Ziegler (361, 362, 365) and of Schlenk and Bergmann (264 to 268) assumes first place. This work has been thoroughly reviewed in recent articles by Wooster (337) and Ziegler (361), and will not be discussed here in detail.

Ziegler and Schlenk and Bergmann have shown that alkali metals, especially sodium and lithium, add to arylolefins of the types

$$\underset{\underset{\textstyle R}{|}}{ArC}{=}CH_2 \qquad Ar_2C{=}CH_2 \qquad \underset{\underset{\textstyle R}{|}}{Ar_2C}{=}CAr \qquad Ar_2C{=}CAr_2 \qquad \underset{\underset{\textstyle R}{|}\ \underset{\textstyle R}{|}}{ArC}{=}CAr$$
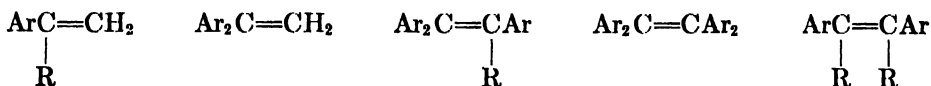
where R is an alkyl group or hydrogen. Lithium frequently adds more readily than does sodium (361), although Gilman (111) found that tetraphenylethylene does not add lithium but does add sodium. Sometimes sodium–potassium alloy gives more rapid addition than does sodium alone (334, 362). Additions which take place but slowly, if at all, in ether, may go more readily in dioxane, or in ether which has been treated with phosphorus pentoxide (178), or in ethylene glycol dimethyl ether (146, 278, 340a).

Alkali metals do not usually add to olefins containing one purely aliphatic-substituted carbon atom (264, 265, 266), such as:

$$ArCH{=}CHR \qquad ArCH{=}CR_2 \qquad Ar_2C{=}CR_2$$

Conant and Blatt (64), however, were able to obtain addition products from dimethylstyrene, $C_6H_5CH{=}C(CH_3)_2$, and 1-phenyl-1-pentene, $C_6H_5CH{=}CHC_3H_7$, with sodium–potassium alloy; and Ziegler and his students were able to add this alloy to dimethyldiphenylethylene $(C_6H_5)_2C{=}C(CH_3)_2$ (362).

The reaction of alkali metals with arylolefins is not always one of simple addition. While stilbene adds sodium smoothly, and hydrolysis of the sodium com-

pound gives the expected dihydro product, its isomer, 1,1-diphenylethylene, adds but one atom of sodium per molecule, and hydrolysis of the intermediate yields a dimer, 1,1,4,4-tetraphenylbutane (265). This dimerizing addition occurs in many cases with unsymmetrical arylolefins (265), and may be considered as analogous to the dimeric reduction of ketones to pinacols by alkali metals. Two interpretations of this reaction have been proposed. Schlenk and Bergmann (267) considered that the addition of the metal to the double bond proceeded stepwise, resulting in the formation of a free radical, which could either dimerize or add a second atom of the metal:

$$(C_6H_5)_2C{=}CHR \rightarrow (C_6H_5)_2\underset{\underset{\bullet}{Na}}{C}{-}CHR$$

$$\nearrow (C_6H_5)_2\underset{Na}{C}{-}\underset{Na}{CHR} \tag{1}$$

$$\searrow (C_6H_5)_2\underset{Na}{CCHRCHRC}(C_6H_5)_2 \tag{2}$$
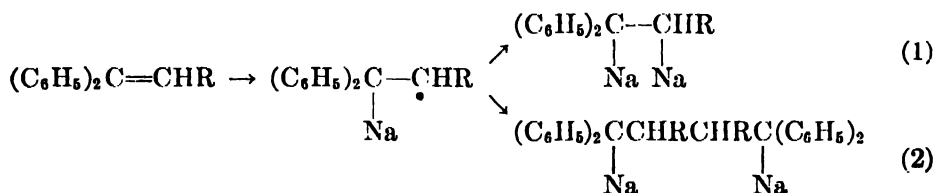
When R is an alkyl group or hydrogen, reaction 2 predominates, but when R is an aryl group, reaction 1 is favored. This mechanism is similar to that proposed by several workers to explain the formation of pinacols from ketones (see section II B).

Ziegler (365), on the other hand, has proposed that the disodium addition product is always formed, but that this can, under suitable conditions, add to a second molecule of the olefin, the more aliphatic part of the organo-alkali compound being the active adding agent:

$$(C_6H_5)_2C{=}CH_2 + 2Na \longrightarrow$$

1,1-Diphenylethylene

$$(C_6H_5)_2\underset{Na}{C}{-}\underset{Na}{CH_2} \xrightarrow{(C_6H_5)_2C{=}CH_2} (C_6H_5)_2\underset{Na}{CCH_2CH_2C}(C_6H_5)_2$$
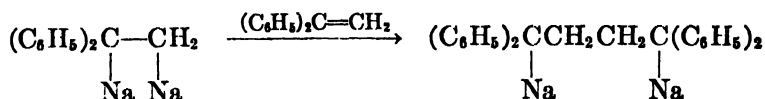
Ziegler (365) has shown that dimerization may be avoided by using an auxiliary substance such as indene or ethylaniline, which replaces the metal in the primary addition product by hydrogen as fast as this is formed. In this way 1,1-diphenylethylene is smoothly reduced to 1,1-diphenylethane without dimerization.

· Dimerization may also occur within a molecule if the structure is favorable. Bergmann (29) has found that 1,1,8,8-tetraphenyl-1,7-octadiene cyclizes on treatment with lithium:

$$(C_6H_5)_2C{=}CHCH_2CH_2CH_2CH_2CH{=}C(C_6H_5)_2 \rightarrow$$

1,1,8,8-Tetraphenyl-1,7-octadiene
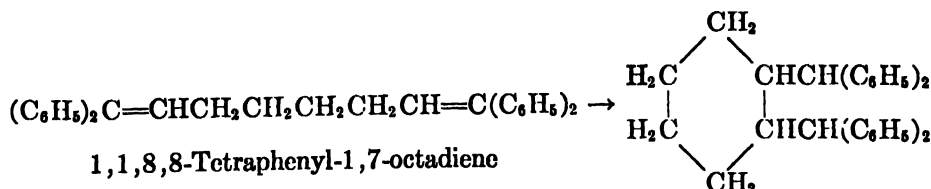
A second abnormal reaction that may occur when an arylolefin is treated with alkali metals in inert solvents is disproportionation, although this does not happen frequently. It has been reported for 1,1-diphenyl-2,2-dimethylethylene (362). This olefin does not add sodium or lithium (266), but with sodium–potassium alloy it undergoes the following reaction:

$$2(C_6H_5)_2C{=}C(CH_3)_2 + 2K \rightarrow (C_6H_5)_2\underset{K}{C}CH(CH_3)_2 + (C_6H_5)_2C{=}\underset{CH_3}{C}{-}CH_2K$$
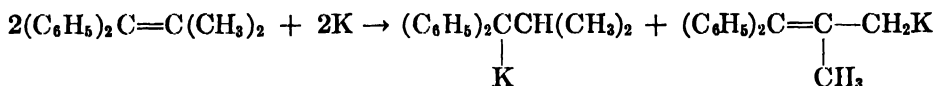
A similar disproportionation has been reported for 1,1-diphenyl-2-benzyl-ethylene (268).

A third abnormal reaction that may occur has been demonstrated by Wittig and Leo (335), and consists of cleavage of an ethane linkage by the alkali metal. This occurred when 1,1,4,4-tetraphenyl-1-butene was treated with potassium, and 1,1,6,6-tetraphenyl-1,5-hexadiene with sodium.

$$(C_6H_5)_2CH{\vert}CH_2CH{=}C(C_6H_5)_2 \xrightarrow{K} (C_6H_5)_2CH_2 + (C_6H_5)_2C{=}CHCH_3$$

$$(C_6H_5)_2C{=}CHCH_2{\vert}CH_2CH{=}C(C_6H_5)_2 \xrightarrow{Na} 2(C_6H_5)_2C{=}CHCH_3$$
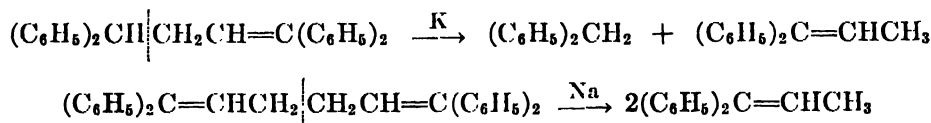
Some of the more sensitive olefins, especially styrene and the aliphatic dienes, are so readily polymerized by alkali metals that the yield of monomeric dihydro compounds is very small when the ordinary procedures are used. This polymerization may be avoided by using an auxiliary substance, such as indene, triphenylmethane, or N-ethylaniline, which reacts with the organo-alkali compound as rapidly as it is formed (364, 365).

$$C_6H_5CH{=}CH_2 + 2Li + 2C_6H_5NHC_2H_5 \longrightarrow C_6H_5CH_2CH_3 + 2C_6H_5\underset{Li}{N}C_2H_5$$
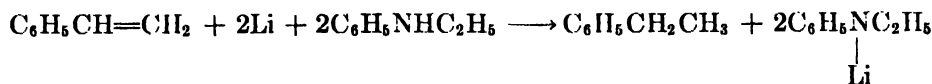
Styrene N-Ethylaniline   Ethylbenzene

The dilithium addition product is probably an intermediate in this reaction, since lithium and ethylaniline do not react with each other under the conditions used.

Lebeau and Picon (184) and Schlubach (269) were among the first to show that arylolefins could be reduced by sodium in liquid ammonia. In recent years this reaction has been studied in considerable detail by Wooster and his coworkers (339) and by Ziegler and his associates (362, 365). Usually the dihydro product is obtained on hydrolysis, but dimerization may occur here as well as with alkali metals in inert media. Ziegler (362) has shown that this dimerization can be avoided by changing the experimental conditions. For example, 1,1-diphenylethylene forms the dimeric compound when sodium is added to a liquid ammonia solution of the olefin, but when the process is reversed, and the olefin is added to an excess of sodium in liquid ammonia, the main product is diphenylethane.

Some olefins that do not add alkali metals in inert solvents are reduced by

sodium in liquid ammonia. Such an olefin is 1,1-diphenyl-2-methylethylene, which, according to Schlenk and Bergmann (265, 266), is not attacked by sodium in ether, but is readily reduced to 1,1-diphenylpropane by sodium in liquid ammonia (339).

In the reduction of arylolefins by alkali metals in liquid ammonia, the metal salt is undoubtedly an intermediate, for it is possible, in some cases at least, to replace at least one of the metal atoms by an alkyl group on treatment with benzyl chloride or ethyl bromide (339). The organo-alkali compounds are, however, frequently extensively ammonolyzed, even at low temperatures (339). In general, the groups RCHNa— and ArCHNa— are more readily ammonolyzed than Ar$_2$CNa—.

Klages and his coworkers (165 to 168) made an extensive study of the reduction of arylolefins by sodium in alcohol. In general, the olefins which readily add alkali metals in inert media are readily reduced by sodium in alcohol, which speaks for a common mechanism for the two reactions. The parallel is not, however, exact, for 1-phenyl-2,2-dimethylethylene reacts with sodium-potassium alloy in ether (64), but it is not reduced by sodium in alcohol (168a).

Very little work appears to have been done with arylolefins and sodium amalgam, but this is certainly a weaker reducing agent than the ones mentioned above, for it is reported that styrene is not reduced by it (291).

Kazanskii and his students have recently developed a new reducing agent, calcium ammonia, Ca(NH$_3$)$_6$, made by passing ammonia vapor over metallic calcium (156). This reducing agent will not attack purely aliphatic olefins such as cyclohexene, but it does reduce arylolefins. The reaction proceeds farther than do reactions with sodium in liquid ammonia, and the aromatic nucleus as well as the side chain is attacked. Styrene is reduced by it to 1-ethylcyclohexene. Allylbenzene, which is not reduced by sodium in alcohol, is reduced by calcium ammonia, to propylcyclohexene. Possibly a rearrangement to propenylbenzene precedes the reduction.

Styrene   1-Ethylcyclohexene
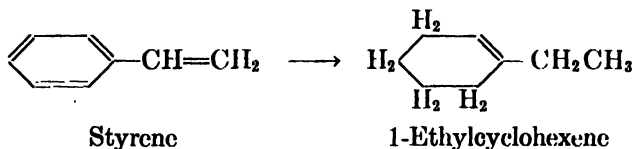
The double bond in the cyclohexene formed in these reductions is always, apparently, on the carbon atom carrying the alkyl side chain.

While the presence of an adjacent aryl group activates an ethylene group sufficiently to permit of reduction by alkali metals, it does not activate it enough for reduction with soluble reducing salts to occur. Karrer, Yen, and Reichstein (150) have shown that while bixin and crocetin can be reduced to the dihydro derivatives with titanium trichloride in ammoniacal solution, this reagent is without effect on styrene, 1,1-diphenylethylene, and tolane. Aluminum amalgam likewise is without action on these compounds (291).

Practically no work has been reported on the reduction of olefins by metals

other than the alkali metals or the alkaline earths. In older work it has been claimed that allyl alcohol can be reduced to propyl alcohol by zinc and sulfuric acid (196) and by aluminum and potassium hydroxide (289), but this has not been confirmed by recent workers. The zinc–copper couple apparently does not bring about reduction of stilbene, for Straus (291) found that the reduction of tolane by this reagent stopped at the stilbene stage. Oleic acid, and other unsaturated acids wherein the double bond is removed from the carboxyl group, can be reduced to the saturated acids by treatment with zinc and acid in the presence of palladium or platinum black (108), but this is probably a case of catalytic hydrogenation.

Some very interesting observations have been made recently by Fuson and his coworkers (10, 11), who have found that 1,2-diaryl-acetylenes and -ethylenes can be reduced at room temperature by benzene and aluminum chloride, forming the diphenylethanes. The mechanism of the reactions is obscure, but it is cer-

TABLE 1

Reduction of arylolefins by benzene and aluminum chloride

COMPOUND REDUCED	PRODUCT
$(p\text{-}ClC_6H_4)_2C{=}CHCOC_6H_5$	$(C_6H_5)_2CHCH_2COC_6H_5$
$(p\text{-}ClC_6H_4)(C_6H_5)C{=}CHCOOH$	$(C_6H_5)_2CHCH_2COOH$
$(C_6H_5)_2C{=}CHCOC_6H_5$	$(C_6H_5)_2CHCH_2COC_6H_5$
$p\text{-}BrC_6H_4CH{=}CHC_6H_5$	$C_6H_5CH_2CH_2C_6H_5$
$(C_6H_5)_2C{=}CHC_6H_5$	$C_6H_5CH_2CH_2C_6H_5$
$C_6H_5CH{=}CHC_6H_5$	$C_6H_5CH_2CH_2C_6H_5$
$p\text{-}ClC_6H_4CH{=}CHC_6H_4Cl$	$C_6H_5CH_2CH_2C_6H_5$
$C_6H_5C{\equiv}CC_6H_5$	$C_6H_5CH_2CH_2C_6H_5$

tainly not merely addition of hydrogen, for substituted aryl groups are replaced by phenyl, and triphenylethylene is converted to dibenzyl. A similar reaction has been reported by Pummerer (251), in which biphenylenediphenylethylene is reduced to the ethane by benzene and aluminum chloride. A summary of Fuson's results is given in table 1.

The most important data on the reduction of olefinic hydrocarbons by chemical reducing agents are summarized in table 2.

D. Reduction of acetylenes

In contrast to simple olefins, acetylenes without aryl or carbonyl groups conjugated to the triple bond can be reduced by chemical reducing agents.

The addition of alkali metals to acetylenes in inert media has not been studied extensively. A German patent to the Bayer Company (28) reports the conversion of dimethylethinylcarbinol to the olefinic alcohol by treatment with sodium in ether, followed by hydrolysis. The yields are reported to be excellent. In contrast to this, Sung Wooseng (293) was able to obtain little if

TABLE 2

Reduction of olefins by chemical reducing agents

COMPOUND REDUCED	REAGENTS AND CONDITIONS	PRODUCTS	REFERENCES
$C_6H_5CH=CH_2$	Na, ether, hydrolysis	Polymers	(264)
	Na (Li), ether, ethylaniline present	$C_6H_5CH_2CH_3$	(364)
	Na, liquid NH_3	$C_6H_5CH_2CH_3$ and polymers	(185a, 339, 102)
	Na amalgam, alcohol	No reduction	(291)
	Na, alcohol	$C_6H_5CH_2CH_3$	(168a)
	$Ca(NH_3)_6$	1-Ethylcyclohexene	(156)
	$TiCl_3$, NH_4OH	No reduction	(150)
$C_6H_5CH_2CH=CH_2$	$Ca(NH_3)_6$	1-Propylcyclohexene	(156)
$C_6H_5CH=CHCH_3$	Na, alcohol	$C_6H_5CH_2CH_2CH_3$	(168a)
$(CH_3)_3C_6H_2CH=CHCH_3$	Na, alcohol	No reduction	(167a)
$C_6H_5CH=CHC_2H_5$	Na, alcohol	$C_6H_5(CH_2)_3CH_3$	(167b)
$C_6H_5CH=CHC_3H_7$	Na–K, ether	$C_6H_5CH_2CHC_3H_7$ $\mid$ $C_6H_5CH_2CHC_3H_7$	(64)
$C_6H_5CH=CHCH(CH_3)C_2H_5$	Na, alcohol	$C_6H_5CH_2CH_2C_4H_9$	(168b)
$C_6H_5CH=C(CH_3)_2$	Na–K, ether	$C_6H_5CH_2C(CH_3)_2$ $\mid$ $C_6H_5CH_2C(CH_3)_2$	(64)
	Na (Li), ether	No reaction	(265)
	Na, alcohol	No reduction	(165a)
$C_6H_5CH=C(C_2H_5)_2$	Na, alcohol	No reduction	(168a)
$C_6H_5C=CH_2$ $\mid$ CH_3	Na, alcohol	$C_6H_5CH(CH_3)_2$	(165a)
$C_6H_5C=CHCH_3$ $\mid$ CH_3	Na, alcohol	$C_6H_5CHC_2H_5$ $\mid$ CH_3	(165a)
$C_6H_5C=CHC_2H_5$ $\mid$ CH_3	Na, alcohol	$C_6H_5CHC_3H_7(n)$ $\mid$ CH_3	(165d)
$C_6H_5C=CHC_3H_7(i)$ $\mid$ CH_3	Na, alcohol	$C_6H_5CHC_4H_9(i)$ $\mid$ CH_3	(168b)
$C_6H_5C=CHC_4H_9(i)$ $\mid$ CH_3	Na, alcohol	$C_6H_5CHC_5H_{11}(i)$ $\mid$ CH_3	(165a)
$C_6H_5C=CHCH_3$ $\mid$ C_2H_5	Na, alcohol	$C_6H_5CHCH_2CH_3$ $\mid$ C_2H_5	(168a)
$C_6H_5C=C(CH_3)_2$ $\mid$ CH_3	Na (Li) ether	No reaction	(265)

TABLE 2—*Continued*

COMPOUND REDUCED	REAGENTS AND CONDITIONS	PRODUCTS	REF- ERENCES
$C_6H_5C{=}C(CH_3)_2$ $\quad\mid$ $\quad C_2H_5$	Na, alcohol	No reduction	(168a)
$C_6H_5C{=}C(CH_3)_2$ $\quad\mid$ $\quad C_3H_7$	Na, alcohol	No reduction	(168a)
$C_6H_5CH{=}CHC_6H_5$	Na (Li), ether	$C_6H_5CH_2CH_2C_6H_5$	(264, 340a)
	Na, liquid NH_3	$C_6H_5CH_2CH_2C_6H_5$	(102)
	Na, alcohol	$C_6H_5CH_2CH_2C_6H_5$	(165b)
$C_6H_5C{=}CHC_6H_5$ $\quad\mid$ $\quad CH_3$	Na, ether	$C_6H_5CHCH_2C_6H_5$ $\quad\mid$ $\quad CH_3$	(267)
	Na, alcohol	$C_6H_5CHCH_2C_6H_5$ $\quad\mid$ $\quad CH_3$	(165b)
$C_6H_5C{=}CHC_6H_5$ $\quad\mid$ $\quad C_2H_5$	Na, alcohol	$C_6H_5CHCH_2C_6H_5$ $\quad\mid$ $\quad C_2H_5$	(167b)
$p\text{-}CH_3C_6H_4CH{=}CHC_6H_4CH_3$	H_2S and heat	Di-p-tolylethane	(17)
$C_6H_5C{=}CC_6H_5$ $\quad\mid\quad\mid$ $\quad H_3C\ \ CH_3$	Na, ether	$C_6H_5CHCHC_6H_5$ $\quad\mid\quad\mid$ $\quad H_3C\ \ CH_3$	(227, 265)
	Na, alcohol	$C_6H_5CHCHC_6H_5$ $\quad\mid\quad\mid$ $\quad H_3C\ \ CH_3$	(227)
$C_6H_5C{=}CHC_6H_5$ $\quad\mid$ $\quad CH_2C_6H_5$	Na, alcohol	$C_6H_5CHCH_2C_6H_5$ $\quad\mid$ $\quad CH_2C_6H_5$	(168a)
$(C_6H_5)_2C{=}CH_2$	Na, ether	$(C_6H_5)_2CHCH_2$ $\qquad\quad\mid$ $(C_6H_5)_2CHCH_2$	(337)
	Na, liquid NH_3, excess sodium	$(C_6H_5)_2CHCH_3$	(362)
	Na, liquid NH_3, excess olefin	$(C_6H_5)_2CHCH_2$ $\qquad\quad\mid$ $(C_6H_5)_2CHCH_2$	(362)
	Na, alcohol	$(C_6H_5)_2CHCH_3$	(165b)
$(C_6H_5C_6H_4)_2C{=}CH_2$	Na, ether	$(C_6H_5C_6H_4)_2CHCH_2$ $\qquad\qquad\mid$ $(C_6H_5C_6H_4)_2CHCH_2$	(265)
$(C_6H_5)_2C{=}CHCH_3$	Na (Li), ether	No reaction	(265)
	Na, K, liquid NH_3	$(C_6H_5)_2CHCH_2CH_3$	(339)
	Na, alcohol	$(C_6H_5)_2CHCH_2CH_3$	(165b)
$(C_6H_5)_2C{=}CHC_2H_5$	Na, ether	No reaction	(266)
	Na, alcohol	Difficult to reduce; obtain $(C_6H_5)_2CHCH_2C_2H_5$	(167b)

TABLE 2—*Concluded*

COMPOUND REDUCED	REAGENTS AND CONDITIONS	PRODUCTS	REF- ERENCES
$(C_6H_5)_2C=CHC_5H_{11}(n)$........	Na, alcohol	$(C_6H_5)_2CHC_5H_{13}(n)$	(167b)
$(C_6H_5)_2C=C(CH_3)_2$...........	Na (Li), ether	No addition	(265)
	K, ether	Disproportionation	(362)
$(C_6H_5)_2C=CHCH_2C_6H_5$.......	Li, ether	Disproportionation	(268)
	Na, liquid NH_3, low tempera- ture	$(C_6H_5)_2CHCH_2CH_2C_6H_5$	(362)
$(C_6H_5)_2C=C(CH_2C_6H_5)_2$.......	Na (Li), ether	No addition	(266)
$(C_6H_5)_2C=CHCH(C_6H_5)_2$.	Na (Li), ether	Complex reaction	(265)
	Na, liquid NH_3	$(C_6H_5)_2CHCH_2CH(C_6H_5)_2$	(339)
$(C_6H_5)_2C=CHC(C_6H_5)_3$.......	Na, butyl alcohol	$(C_6H_5)_2CHCH_2C(C_6H_5)_3$	(169)
	Li, ether	$(C_6H_5)_3CH$ and $(C_6H_5)_2$- $CHCH=CHCH(C_6H_5)_2$	(169)
$(C_6H_5)_2C=CHC_6H_5$...........	Na (Li), ether	$(C_6H_5)_2CHCH_2C_6H_5$	(265)
	Na (K), liquid NH_3	$(C_6H_5)_2CHCH_2C_6H_5$	(339)
$(C_6H_5)_2C=CC_6H_5$ $\mid$ CH_3.............	Na, ether	$(C_6H_5)_2CHCHC_6H_5$ $\mid$ CH_3	(265)
$(C_6H_5)_2C=C(C_6H_5)_2$...........	Na, ether	$(C_6H_5)_2CHCH(C_6H_5)_2$	(265)
	Li, K, ether	No addition	(111)
	Na, liquid NH_3	$(C_6H_5)_2CHCH(C_6H_5)_2$	(339)
	Al amalgam	No reduction	(298)

any reduction of various carbinols of the formula

$$\begin{array}{c} R_2 \\ \mid \\ R_1-C-C\equiv CH \\ \mid \\ OH \end{array}$$

by treatment with sodium in ether. Tolane reacts very slowly with sodium in ether, and the product is chiefly a mixture of polymers (265), but it reacts with lithium in ether more readily. Bergmann (31, 33) isolated triphenylnaphthalene from the reaction mixture after hydrolysis, but Smith and Hoehn (288) have recently shown that the primary product is tetraphenylbutadiene, which must result from a dimeric addition of lithium similar to that obtained in the case of 1,1-diphenylethylene. In the presence of excess lithium the tetraphenylbutadiene is converted to triphenylnaphthalene:

Tolane   Tetraphenylbutadiene

Triphenylnaphthalene

Sodium in liquid ammonia was early observed to cause reduction of acetylene and its alkyl derivatives. Moissan (215, 216), in a study of the preparation of alkali acetylides, found that acetylene reacted with sodium, potassium, cesium, and rubidium in liquid ammonia in accordance with the following equation:

$$3HC\equiv CH + 2Me \longrightarrow 2HC\equiv CMe + CH_2=CH_2$$

A similar observation was made by Lebeau and Picon (185) for monoalkylacetylenes. They found that these hydrocarbons reacted with sodium in liquid ammonia to give 2 moles of the sodium alkylacetylide and 1 mole of olefin, and for this reason they advocated the use of sodium amide for preparing the acetylide salts of alkylacetylenes. Phenylacetylene on treatment with sodium in liquid ammonia yields, not styrene, but ethylbenzene (185a). Recent work by Campbell and Eby (56, 57) has shown that both mono- and di-alkylacetylenes can be reduced to the corresponding olefins, in excellent yields, by sodium in liquid ammonia, and that this is one of the best means of preparing olefins of known position of the double bond, for the olefin is not contaminated by any saturated hydrocarbon. The method can also be used with branched-chain acetylenes, such as 3,3-dimethyl-4-nonyne (60), and with acetylenic carbinols (57). In the case of dialkylacetylenes, *trans* olefins are formed. Lithium has been found to give the same results as sodium.
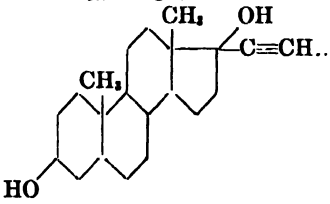
Sodium in alcohol is not as efficient a reducing agent for acetylenes as is sodium in liquid ammonia. It will reduce tolane to stilbene (291), but it is without effect on mono- and di-alkylacetylenes. Bourguel (43) reported that tetramethylbutynediol was reduced by this reagent to the *trans* ethylenic glycol. Subsequent work by Zalkind (348) and by Johnson (147a) has shown this to be incorrect; the product is a polymorphic form of the acetylene glycol, and no reduction takes place. Sodium amalgam has not been much used, but it appears to be too weak, as phenylacetylene is not attacked by it in the cold (291), nor is tolane (16).

Some acetylenes can be reduced by zinc dust, either in acid or basic solution, or by the zinc–copper couple in neutral solution. Dimethylethinylcarbinol is converted to the ethylenic carbinol by zinc and acetic acid or by the zinc–copper couple (28), and acetylene, phenylacetylene, mono- and di-vinylacetylenes, and propiolic acid are said to be reduced to the corresponding olefins by the zinc–copper couple (87, 88), or by zinc in basic solution. Straus (291) found that

TABLE 3

Reduction of acetylenes by chemical reducing agents

COMPOUND REDUCED	REAGENTS AND CONDITIONS	PRODUCTS	REFER-ENCES
$HC\equiv CH$	Na, liquid NH_3 (also K, Cs, Rb)	$CH_2=CH_2$ and $CH\equiv CNa$	(215, 216)
	Zn–Cu, H_2O	$CH_2=CH_2$	(88)
	Cr^{++} in acid or NH_4OH solution	$CH_2=CH_2$	(303)
$RC\equiv CH$ (where R = normal alkyl up to C_6)	Na, liquid NH_3	$RCH=CH_2$	(185, 57)
$RC\equiv CR'$ (where R and R' are normal alkyl groups)	Na or Li, liquid NH_3	$RCH=CHR'$	(56, 57)
$(CH_3)_2CC\equiv CH$ $\mid$ OH	Na, ether		(28)
	Zn, acetic acid	$(CH_3)_2CCH=CH_2$ $\mid$ OH	(28)
	Zn–Cu couple		(28, 88)
$\quad CH_3$ $\quad \mid$ $C_2H_5CC\equiv CH$ $\quad \mid$ $\quad OH$	Na, liquid NH_3	$\quad CH_3$ $\quad \mid$ $C_2H_5CCH=CH_2$ $\quad \mid$ $\quad OH$	(57)
$\quad R_2$ $\quad \mid$ $R_1CC\equiv CH$ $\quad \mid$ $\quad OH$ $\{R_1 = CH_3$ and $R_2 = t\text{-}C_4H_9$ $\{R_1 = R_2 = n\text{-}C_3H_7$ $\{R_1 = CH_3$ and $R_2 = i\text{-}C_3H_7$	Na, ether Mg amalgam, CH_3-OH Fe, acetic acid Mg, acetic acid	Little or no reduction	(293)
$\quad\quad CH_3$ $\quad\quad \mid$ $HC\equiv CCCH_2CH_2CH=C(CH_3)_2$ $\quad\quad \mid$ $\quad\quad OH$	Na, moist ether	$\quad\quad CH_3$ $\quad\quad \mid$ $CH_2=CHCCH_2CH_2CH=C(CH_3)_2$ $\quad\quad \mid$ $\quad\quad OH$ Linaloöl	(258a) (258a)
$(CH_3)_2CC\equiv CC_4H_9(n)$ $\mid$ OH	Na, liquid NH_3	$(CH_3)_2CCH=CHC_4H_9$ $\mid$ OH	(57)
$(CH_3)_2CC\equiv CC(CH_3)_2$ $\mid\quad\quad\quad\mid$ $OH\quad\quad OH$	Na, alcohol	No reduction	(348, 147a)

TABLE 3—*Concluded*

COMPOUND REDUCED	REAGENTS AND CONDITIONS	PRODUCTS	REFERENCES
$C_6H_5C{\equiv}CH$	Na amalgam, cold	No reduction	(291)
	Zn, acetic acid	$C_6H_5CH{=}CH_2$	(16)
	Zn–Cu	$C_6H_5CH{=}CH_2$ and $C_6H_5CH{=}CHCH{=}CHC_6H_5$	(291)
	Zn with Cu or Cd	$C_6H_5CH{=}CH_2$	(88)
	Zn, basic solution	$C_6H_5CH{=}CH_2$	(87)
$C_6H_5C{\equiv}CC_6H_5$	Na, ether	Slow reaction; polymers formed	(265)
	Li, ether	$[(C_6H_5)_2C{=}CH{-}]_2$ and 1,2,3-triphenylnaphthalene	(31, 265, 288)
	Na, methanol	*trans*-Stilbene	(16)
	Na, ethanol	$C_6H_5CH_2CH_2C_6H_5$	(16)
	Na amalgam	No reduction	(16)
	Zn, acetic acid	*trans*-Stilbene	(16)
	Zn–Cu, alcohol	*cis*-Stilbene	(291)
	C_6H_6, $AlCl_3$	$C_6H_5CH_2CH_2C_6H_5$	(11)
$(C_6H_5)_2CC{\equiv}CC(C_6H_5)_2$ $\quad\mid\qquad\mid$ $\quad OH\quad\ OH$	Na, alcohol	No reduction	(345)
$(C_6H_5)_2CC{\equiv}CCHC_6H_5$ $\quad\mid\qquad\mid$ $\quad OH\quad\ OH$	Na, alcohol	No reduction	(345)
	Na, xylene, alcohol	Olefin	(117)

phenylacetylene on treatment with zinc and alcohol formed styrene chiefly, but also a little phenylbutadiene. This may possibly be a dimerizing reduction similar to that found with arylolefins and sodium. Sung Wooseng (293) was unable to reduce tertiary acetylenic carbinols with magnesium amalgam, or with iron or magnesium and acetic acid.

No work appears to have been done on the reduction of acetylenic hydrocarbons by calcium ammonia, but since this reagent will attack a benzene ring, it is probable that it will reduce acetylenes also. The action of soluble metal

salts on acetylenic hydrocarbons has received but little attention. Traube (303) found that acetylene itself could be reduced to ethylene in good yield by chromous chloride in acid or in ammoniacal solution, but Karrer (150) observed that titanium trichloride is not a strong enough reducing agent to attack tolane, although it will bring about the reduction of some conjugated compounds.

The data on the reduction of acetylenes by chemical methods are summarized in table 3. The work on the stereochemical course of reduction of disubstituted acetylenes is discussed in section II F.

E. Reduction of polyunsaturated hydrocarbons

1. Reduction of conjugated dienes and polyenes

In contrast to a simple ethylenic group, a system of two or more such groups united in a conjugated chain is reducible by dissolving metal combinations, and in this respect the conjugated diene hydrocarbons resemble the acetylenes and arylolefins. They are, in fact, more easily reduced, since most of them are attacked by sodium amalgam in the cold, and the polyenes and some of the aryl dienes are reduced by aluminum amalgam, a reagent which is without effect on acetylenes, arylolefins, and purely aliphatic dienes (291, 333).

Alkali metals in inert media cause rapid polymerization of phenylbutadiene and the aliphatic dienes such as butadiene, isoprene, and dimethylbutadiene (361, 364); this reaction was of importance in the early development of synthetic rubber. Ziegler and his coworkers (361) considered that the primary product is an organo-alkali compound, formed by the addition of two atoms of the metal to one molecule of the diene. This organo-alkali compound can then add to unreacted diene, forming a new organo-alkali compound. By repetition of this process, polymers of very high molecular weight can be obtained. The addition occurs in the 1,4-positions, for Midgley and Henne (213) demonstrated that the dimerization of isoprene by potassium led to three dimethyloctadienes, as shown below:

$$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{\underset{\underset{CH_3}{|}}{C}}{=}\overset{4}{C}H_2 \; + \; \left[\overset{1}{C}H_2\overset{2}{C}H{=}\overset{3}{\underset{\underset{CH_3}{|}}{C}}{-}\overset{4}{C}H_2\right]^{--} K_2^{++} \; \xrightarrow{\;H_2O\;}$$

Isoprene

$$\left\{ \begin{array}{l} CH_3CH{=}\underset{\underset{CH_3}{|}}{C}CH_2CH_2CH{=}\underset{\underset{CH_3}{|}}{C}CH_3 \\[3ex] CH_3CH{=}\underset{\underset{CH_3}{|}}{C}CH_2CH_2\underset{\underset{CH_3}{|}}{C}{=}CHCH_3 \\[3ex] CH_3\underset{\underset{CH_3}{|}}{C}{=}CHCH_2CH_2CH{=}\underset{\underset{CH_3}{|}}{C}CH_3 \end{array} \right.$$
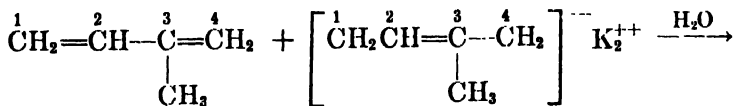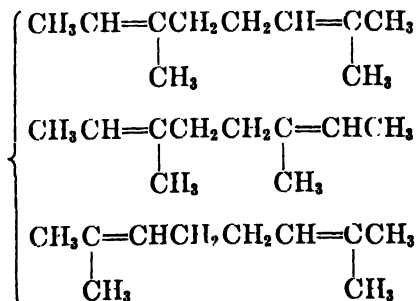
Ziegler and his students (363, 364) have shown that the polymerizing action of alkali metals on aliphatic dienes can be avoided, as in the case of styrene, by the use of ethylaniline (or other substances with acidic hydrogen atoms, such as fluorene and triphenylmethane), which reacts with the metallic addition product as fast as this is formed, and before it has time to react with the unused diene. In this way dihydro compounds are readily obtained from butadiene, isoprene, and 2,3-dimethylbutadiene.

$$\underset{\underset{Li}{\vert}}{RCHCH}=\underset{\underset{Li}{\vert}}{CHCHR} + 2C_6H_5NHC_2H_5 \longrightarrow$$

$$RCH_2CH=CHCH_2R + 2C_6H_5\overset{-}{N}C_2H_5$$
$$\underset{Li^+}{\vert}$$
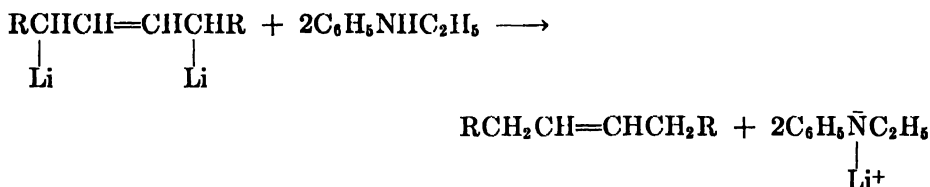
The carotenoids and diarylpolyenes react very slowly with sodium in ether, but the addition of lithium in dioxane occurs much more rapidly (178). When addition reactions are carried out in ether, they occur more easily if the ether has been treated with phosphorus pentoxide (178).

The course of the reduction of conjugated hydrocarbons by alkali metals is of considerable interest. According to Thiele's theory (296), it should always occur at the ends of the conjugated chain, but recent work indicates that this is not always the case. If Burton and Ingold's mechanism be applied (54), the nature and position of substituents would be of great importance in determining the mode of addition, by causing one form of the intermediate ion to predominate over the other. In a symmetrical molecule, especially one in which the end atoms of the conjugated chain are linked to electron-attracting groups, terminal addition of hydrogen should occur exclusively. In unsymmetrical molecules, it would be predicted that varying amounts of terminal and non-terminal addition would take place.

$$RCH=CH-CH=CHY + 2e + H^+ \longrightarrow$$

$$RCH=CH-\overset{-}{C}H-CH_2Y \overset{H^+}{\longrightarrow} RCH=CHCH_2CH_2Y$$
$$\Updownarrow$$
$$R\overset{-}{C}H-CH=CH-CH_2Y \overset{H^+}{\longrightarrow} RCH_2CH=CHCH_2Y$$
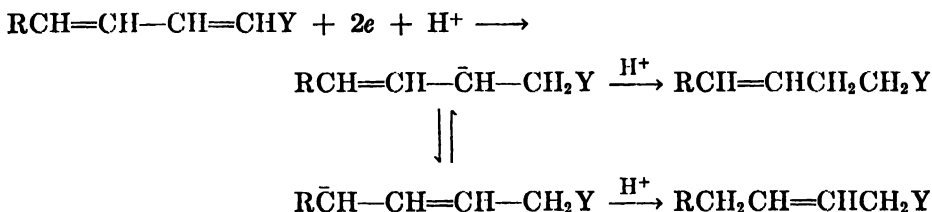
The reduction of carotenoids and α,ω-diarylpolyenes by sodium amalgam or aluminum amalgam, or by the addition of alkali metals in inert media followed by hydrolysis, leads to the addition of hydrogen at the ends of the conjugated chain, and the reaction stops at the dihydro stage, even though the product itself contains a conjugated system (177, 178, 334). With sodium amalgam the diphenylpolyenes also give some oily products, and the initial product may undergo rearrangement, whereas aluminum amalgam does not cause such rearrangement (177).

$$
\begin{array}{c}
C_6H_4 \\
\diagdown \\
\text{C}=\text{CH}-\text{CH}=\text{CHC}_6H_5 \\
\diagup \\
C_6H_4 \\
\text{Cinnamalfluorene}
\end{array}
\xrightarrow[\text{Na(Hg)}_2]{\text{Al(Hg)}_x}
\begin{array}{c}
C_6H_4 \\
\diagdown \\
\text{CH}-\text{CH}=\text{CH}-\text{CH}_2C_6H_5 \\
\diagup \\
C_6H_4
\end{array}
\xrightarrow{\text{Na(Hg)}_2}
\begin{array}{c}
C_6H_4 \\
\diagdown \\
\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2C_6H_5 \\
\diagup \\
C_6H_4
\end{array}
$$
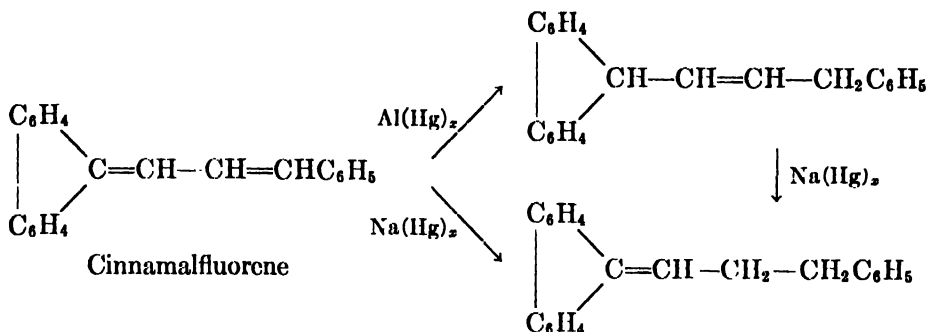
This same hydrocarbon, cinnamalfluorene, adds sodium in ether to form the dimeric addition product (265).

$$
\begin{array}{ccc}
C_6H_4 & & C_6H_4 \\
\diagdown & & \diagup \\
\text{CH}-\text{CH}-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\text{CH}-\text{CH} & & \\
\diagup\;\;\;| & \qquad\quad | \;\;\;\diagdown & \\
C_6H_4\;\; \text{CH}=\text{CHC}_6H_5 & C_6H_5\text{CH}=\text{CH}\;\;C_6H_4 &
\end{array}
$$
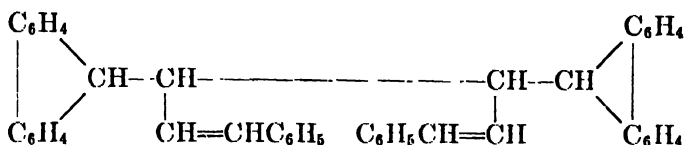
Thiele (299) also obtained some dimer upon the reduction of cinnamalfluorene with aluminum amalgam.

Other symmetrically substituted diaryldienes are reduced in the terminal positions by the reagents mentioned above. 1,1,4,4-Tetraphenylbutadiene adds lithium in the terminal positions (38) and is reduced by sodium amalgam to 1,1,4,4-tetraphenyl-2-butene (265a), but on treatment with sodium in amyl alcohol it is reduced to the tetraphenylbutane (307); this reaction indicates that the terminal dihydro compound is rearranged by the alkali and higher temperature to 1,1,4,4-tetraphenyl-1-butene, which is then further reduced. 1,1,6,6-Tetraphenylhexatriene slowly adds sodium or lithium (potassium more rapidly), and hydrolysis gives 1,1,6,6-tetraphenyl-2,4-hexadiene (334). Allen (12) found that 2,3-diphenylbutadiene is completely reduced by sodium in liquid ammonia, a fact that is not surprising, for the 1,4-reduction product would be dimethylstilbene, which is itself reduced by alkali metals. 1,2,3,4-Tetraphenylbutadiene adds sodium in the 1,4-positions, and is difficultly reduced to the 1,4-dihydro compound by sodium in alcohol, the reaction stopping at this stage (32), although it would be expected that the dihydro compound would be easily reduced further by alkali metals.

Very little work has been reported on the course of the reduction of unsymmetrical aryldienes. It is here, however, that one would expect non-terminal addition to occur most extensively. 1-Phenylbutadiene, according to Klages (165), is reduced terminally by sodium in alcohol, although 1-phenyl-3-methylbutadiene is reported to give a 1,2-dihydro compound. Conclusive proof of these structures is, however, lacking.

With purely aliphatic dienes, such as butadiene, isoprene, and 2,3-dimethylbutadiene, addition of alkali metals (363, 364) and reduction by these metals

in reactive solvents tend to occur exclusively in the 1,4-positions (130, 212, 213); sometimes dimers and polymers are also formed.

Two cases have been reported in which the reduction of an aliphatic polyene does not occur exclusively in the terminal positions. Dupont and his coworkers (77) studied the reduction of alloöcimene in detail, using Raman-spectra data among other evidence to establish the structures of the products. With sodium in liquid ammonia alloöcimene forms a dihydro product which is a homogeneous substance and contains a conjugated system. It has been shown to be 2,6-dimethyl-3,5-octadiene (II), and it is reduced further to 2,6-dimethyl-1-octene (III) by sodium in liquid ammonia.

$$CH_3C{=}CHCH{=}CHC{=}CHCH_3 \longrightarrow CH_3CHCH{=}CHCH{=}CCH_2CH_3 \longrightarrow$$
$$\quad\;\; | \qquad\qquad\quad | \qquad\qquad\qquad\quad | \qquad\qquad\qquad\quad |$$
$$\quad\; CH_3 \qquad\qquad CH_3 \qquad\qquad\qquad CH_3 \qquad\qquad\quad CH_3$$

I
Alloöcimene

II
2,6-Dimethyl-3,5-octadiene

$$CH_3CHCH_2CH{=}CHCHCH_2CH_3$$
$$\quad\; | \qquad\qquad\qquad |$$
$$\quad\, CH_3 \qquad\qquad CH_3$$

III
2,6-Dimethyl-4-octene
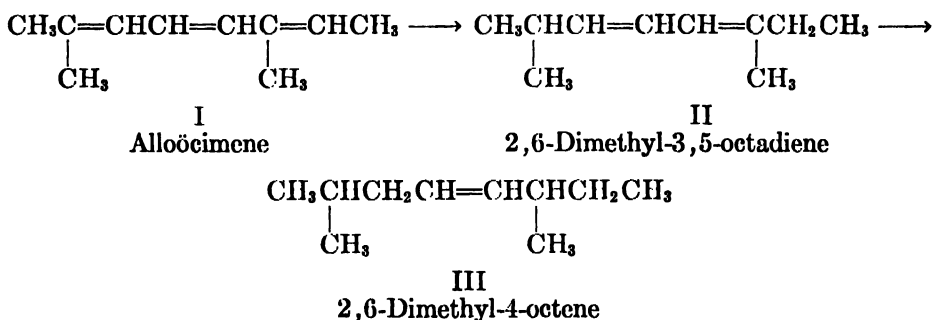
When alloöcimene is reduced by sodium and alcohol, however, the product is not identical with II, and is not homogeneous. From Raman spectra and reduction experiments Dupont and coworkers concluded that it is an approximately equimolar mixture of II and the 3,6-reduction product,

$$(CH_3)_2C{=}CHCH_2CH{=}CCH_2CH_3$$
$$\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\; CH_3$$
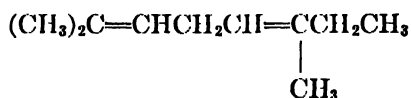
which does not contain a conjugated system.

In a similar fashion, Dupont and Desreux (75, 76) have shown that while reduction of β-myrcene by sodium in alcohol occurs largely in the 1,4-positions, as reported by Semmler (279), it does not do so exclusively, and there is also some 1,2-dihydro product formed.

$$CH_3CH{=}CCH_2CH_2CH{=}C(CH_3)_2$$
$$\qquad\qquad | $$
$$\qquad\quad CH_3$$
(main product)

$$CH_2{=}CHCCH_2CH_2CH{=}C(CH_3)_2 -\!\!\prec$$
$$\qquad\quad \|$$
$$\qquad\; CH_2$$

β-Myrcene

$$CH_3CH_2CCH_2CH_2CH{=}C(CH_3)_2$$
$$\qquad\qquad \|$$
$$\qquad\quad CH_2$$
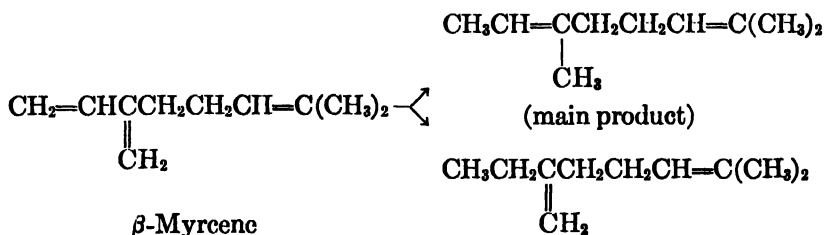
It is possible that a careful reëxamination of the reduction products from other unsymmetrical dienes will reveal additional cases where terminal reduction is not the sole reaction.

While most of the reduction studies on conjugated hydrocarbons have been made with alkali metals, in a few cases other reducing agents have been used. As mentioned earlier, aluminum amalgam will bring about the reduction of the α,ω-diphenylpolyenes (177) and of cinnamalfluorene (177, 298); it is without action, however, on 1,4-diphenylbutadiene (291) and on aliphatic dienes and polyenes (333). Calcium ammonia in the cold reduces conjugated dienes to olefins, and the reaction stops at this point; the product, apparently, is formed by 1,4-addition of hydrogen, for 2,3-dimethylbutadiene gives tetramethylethylene (156). Dienes with isolated double bonds are also attacked by this reagent; possibly it causes isomerization to a conjugated form, which is then reduced. 2,5-Dimethyl-1,5-hexadiene is thus converted to 2,5-dimethyl-3-hexene.

The simple aryl-substituted dienes are not reduced by the zinc–copper couple (291), but long-chain conjugated polyenes terminating in a carbonyl group are reduced to the α,ω-dihydro derivatives by zinc and acetic acid (172).
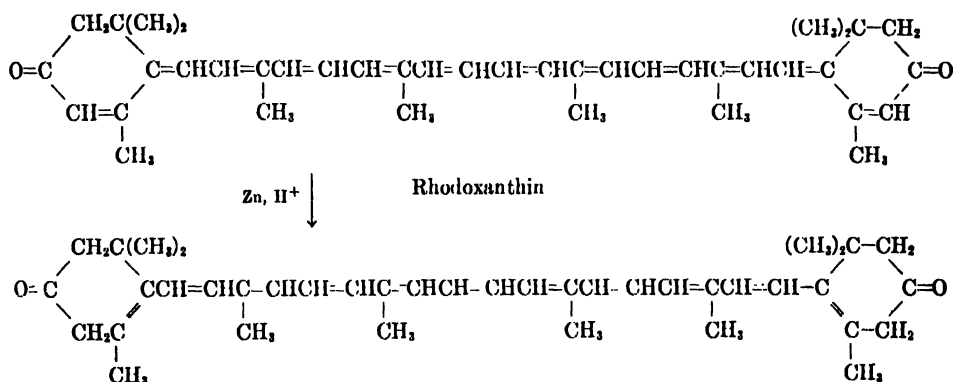
An interesting case of the reduction of polyenes has recently been observed by Fischer and Wiedmann (107), who found that diene alcohols (with primary hydroxyl groups) are reduced by certain fermenting yeasts, the double bond adjacent to the alcohol group being the one attacked.

$$CH_3CH{=}CHCH{=}CHCH{=}CHCH_2OH \;\to$$

$$CH_3CH{=}CHCH{=}CHCH_2CH_2CH_2OH$$
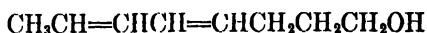
The corresponding acid and aldehyde are also reduced to the same product.

Karrer and his students (149, 150) have shown that polyene hydrocarbons are not reduced by titanium trichloride in ammoniacal solution; the presence of a carboxyl or carbonyl group is essential.

In table 4 the data for the chemical reduction of conjugated hydrocarbons are recorded. A discussion of the stereochemical aspect of the reduction of conjugated substances is included in section II F.
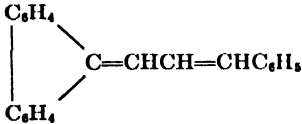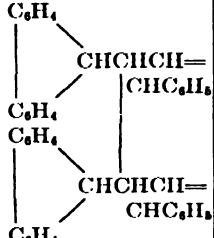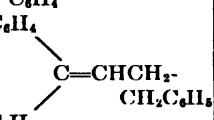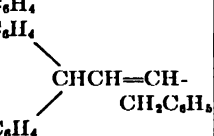
2. Reduction of enynes and diynes

Comparatively little work has been done on the reduction of these substances. Straus (291) made a detailed investigation of the reduction of diphenyldiacety-

TABLE 4

Reduction of conjugated diene and polyene hydrocarbons

COMPOUND REDUCED	REDUCING AGENTS AND CONDITIONS	PRODUCTS	REFER-ENCES
Butadiene.............................. CH_2=CHCH=CH_2	Na, ether	Polymers	(364)
	Na, ether, ethylaniline	*cis*-2-Butene	(363)
	Na (Ca), liquid NH_3	2-Butene and dimer	(130)
Isoprene.............................. CH_2=CHC=CH_2 $\quad\quad\mid$ $\quad\quad CH_3$	Na, ether	Polymers	(364)
	Na, liquid NH_3 (excess sodium)	2-Methyl-2-butene	(212)
	K, alcohol	Dimers; 2,6-, 2,7-, and 3,6-dimethyl-2,6-octadienes	(213)
Dimethylbutadiene.................... CH_2=C—C=CH_2 $\quad\quad\mid\quad\mid$ $\quad H_3C\quad CH_3$	Na (Li), ether	3 per cent tetramethylethylene, 60 per cent 2,3,6,7-tetramethyl-2,6-octadiene	(364)
	Na (Li), ether, ethylaniline	Tetramethylethylene	(363)
	K, alcohol	2,3,6,7-Tetramethyl-2,6-octadiene; higher polymers	(213)
	Ca(NH_3)$_6$	Tetramethylethylene	(156)
Piperylene............................. CH_2=CHCH=CHCH$_3$	Li, ether	Polymers	(364)
	Na, ether, triphenylmethane	Hexamers and higher polymers	(364)
5-Methyl-2,4-heptadiene................ CH_3CH=CHCH=CCH$_2$CH$_3$ $\quad\quad\quad\quad\quad\quad\mid$ $\quad\quad\quad\quad\quad\quad CH_3$	Na, liquid NH_3	5-Methyl-3-heptene (largely *trans*)	(77)
Alloöcimene........................... (CH_3)$_2$C=CHCH=CHC=CHCH$_3$ $\quad\quad\quad\quad\quad\quad\quad\quad\mid$ $\quad\quad\quad\quad\quad\quad\quad\quad CH_3$	Na, alcohol	2,6-Dimethyl-3,5-octadiene and 2,6-dimethyl-2,5-octadiene	(77)
	Na, liquid NH_3	2,6-Dimethyl-3,5-octadiene	(77)
β-Myrcene............................. CH_2=CHCCH$_2$CH$_2$CH=C(CH$_3$)$_2$ $\quad\quad\mid\mid$ $\quad\quad CH_2$	Na, alcohol	Chiefly 3,7-dimethyl-2,6-octadiene; some 2-ethyl-6-methyl-1,5-heptadiene	(75, 76, 279)
1,3-Cyclohexadiene....................	Ca(NH_3)$_6$	Cyclohexene	(156)
4,6-Dimethyl-1,3-cyclohexadiene........	Na, alcohol	4,6-Dimethyl-2-cyclohexene	(21)

TABLE 4—*Continued*

COMPOUND REDUCED	REDUCING AGENTS AND CONDITIONS	PRODUCTS	REFER- ENCES
Carotenoids..........................	Al amalgam	α,ω-Dihydro compounds	(151, 178)
1-Phenylbutadiene..................... $C_6H_5CH=CHCH=CH_2$	Na, alcohol	1-Phenyl-2-butene	(165c)
1-Phenyl-3-methylbutadiene............ $C_6H_5CH=CHC=CH_2$ $\quad\quad\quad\quad\mid$ $\quad\quad\quad\quad CH_3$	Na, alcohol	1-Phenyl-3-methyl-3-butene	(165c)
1,4-Diphenylbutadiene................. $C_6H_5CH=CHCH=CHC_6H_5$	Na (Li), ether	*cis*-1,4-Diphenyl-2-butene	(265a)
	Na amalgam, alcohol	*trans*-1,4-Diphenyl-2-butene	(291, 265a)
	Al amalgam	No reduction	(298)
	Zn–Cu, alcohol	No reduction	(291)
ArCH=CHCH=CHAr, where Ar is $\}$.... p-tolyl or p-anisyl	Na, amyl alcohol	$ArCH_2CH_2CH_2CH_2Ar$	(46)
Cinnamalfluorene....................... $\quad C_6H_4$ $\quad\mid$ $\quad\quad\quad C=CHCH=CHC_6H_5$ $\quad\mid$ $\quad C_6H_4$	Na (Li), ether	Dimer, $\quad C_6H_4$ $\quad\quad\quad\quad\quad CHCHCH=$ $\quad\quad\quad\quad\quad\quad\mid CHC_6H_5$ $\quad C_6H_4$ $\quad C_6H_4$ $\quad\quad\quad\quad\quad CHCHCH=$ $\quad\quad\quad\quad\quad\quad CHC_6H_5$ $\quad C_6H_4$	(265)
	Na amalgam	C_6H_4 $\quad\quad\quad\quad C=CHCH_2-$ $\quad\quad\quad\quad\quad CH_2C_6H_5$ C_6H_4	(177)
	Al amalgam	C_6H_4 $\quad\quad\quad\quad CHCH=CH-$ $\quad\quad\quad\quad\quad CH_2C_6H_5$ C_6H_4	(298, 177)
2,3-Diphenylbutadiene.................. $CH_2=C\text{——}C=CH_2$ $\quad\quad\mid\quad\quad\mid$ $\quad\quad C_6H_5\ C_6H_5$	Na, liquid NH$_3$	meso 2,3-Diphenyl-butane	(12)
	Na amalgam	No reduction	(12)
1,1,4,4-Tetraphenylbutadiene........... $(C_6H_5)_2C=CHCH=C(C_6H_5)_2$	Na (Li), ether	*trans*-1,1,4,4-Tetraphenyl-2-butene	(265a)
	Na, amyl alcohol	Tetraphenylbutane	(307)
	Na amalgam, alcohol	*trans*-1,1,4,4-Tetraphenyl-2-butene	(265a)
1,2,3,4-Tetraphenylbutadiene .... $C_6H_5CH=C\text{——}C=CHC_6H_5$ $\quad\quad\quad\mid\quad\quad\mid$ $\quad\quad\quad C_6H_5\ C_6H_5$	Na, ether	1,2,3,4-Tetraphenyl-2-butene and an indene derivative	(32)
	Na, amyl alcohol	1,2,3,4-Tetraphenyl-2-butene and an indene derivative	(32)
	Al amalgam	No reduction	(32)

TABLE 4—*Concluded*

COMPOUND REDUCED	REDUCING AGENTS AND CONDITIONS	PRODUCTS	REFER-ENCES
α,ω-Diphenylpolyenes, $C_6H_5(CH{=}CH)_n$-C_6H_5, where n is more than 2........	Na (Li), ether or dioxane	α,ω-Dihydro (slowly)	(177)
	Na amalgam	α,ω-Dihydro	(177, 178)
	Al amalgam	α,ω-Dihydro; some polymers	(177)
	Na, alcohol	α,ω-Dihydro	(177, 178)
1,1,6,6-Tetraphenylhexatriene. .... $(C_6H_5)_2C{=}CHCH{=}CHCH{=}C(C_6H_5)_2$	Na (Li), dioxane	1,1,6,6-Tetraphenyl-2,4-hexadiene (slowly)	(334)
	NaK alloy, dioxane	1,1,6,6-Tetraphenyl-2,4-hexadiene and 1,1,6,6-tetra-phenyl-1,3-hexa-diene	(334)

lene by means of the zinc-copper couple and alcohol. The reaction takes place stepwise, and the initial product was considered by Straus to be a labile form of diphenylbutenyne, but Grignard and Tchéoufaki (126) have shown by ozonolysis that it is diphenylbutatriene; hence the reduction takes place in the 1,4-positions. The butatriene rearranges in the presence of iodine to the butenyne, and both of these are reduced further to diphenylbutadiene by the zinc-copper couple.

$$C_6H_5C{\equiv}C{-}C{\equiv}CC_6H_5 \xrightarrow{Zn\text{-}Cu} C_6H_5CH{=}C{=}C{=}CHC_6H_5 \rightarrow C_6H_5CH{=}CHCH{=}CHC_6H_5$$

Diphenyldiacetylene

(labile, *cis-cis*)

$\downarrow I_2$

$$C_6H_5C{\equiv}C{-}CH{=}CHC_6H_5 \rightarrow C_6H_5CH{=}CHCH{=}CHC_6H_5$$

(*cis-trans*)

$\downarrow$ light

$$C_6H_5CH{=}CHCH{=}CHC_6H_5 \leftarrow$$

(stable, *trans-trans*)

Aluminum amalgam does not reduce diphenyldiacetylene (291).

Conjugated enynes are reduced by zinc in neutral or basic solution, and the triple bond seems to be attacked first, for the product is the conjugated diene. Thus, vinylacetylene, on treatment with zinc in sodium hydroxide solution (87) or with the zinc-copper couple in alcohol solution, forms 1,3-butadiene. Table 5 includes the data on this subject.

3. Reduction of hydrocarbons containing crossed conjugated systems

The most widely studied compounds containing this sytem are the fulvenes

(I), the benzofulvenes (II), and the dibenzofulvenes (III).   Practically all of these are capable of reacting with sodium in inert media (39, 265).
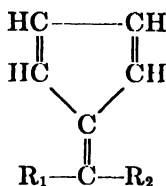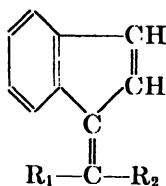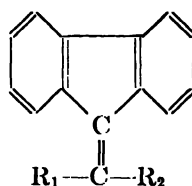
| I | II | III |
| Fulvenes | Benzofulvenes | Dibenzofulvenes |

TABLE 5

Chemical reduction of enynes and diynes

COMPOUND	REDUCING AGENTS	PRODUCTS	REFERENCES
Vinylacetylene .... CH_2=CHC≡CH	Zn powder, NaOH	Butadiene	(87, 133)
	Zn–Cu couple, alcohol	Butadiene	(88, 192)
Diphenylvinylacetylene....... C_6H_5CH=CHC≡CC$_6$H$_5$	Zn–Cu couple, alcohol	Diphenylbutadiene	(291)
Divinylacetylene............. CH_2=CHC≡CCH=CH$_2$	Zn–Cu couple, alcohol	1,3,5-Hexatriene	(88)
Diacetylene................. HC≡CC≡CH	Zn–Cu couple, alcohol	Butadiene	(88)
Diphenyldiacetylene......... C_6H_5C≡CC≡CC$_6$H$_5$	Na (Li), ether	Polymers	(265)
	Zn–Cu couple, alcohol	Diphenylbutatriene, C_6H_5CH=C=CH-C$_6$H$_5$, and 1,4-diphenyl-1,3-butadiene	(291, 126)

When both R groups are alkyl, the product is a dimer:
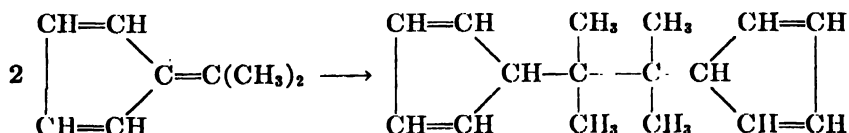
When both R groups are aromatic, a monomeric dihydro compound is formed, and when one R group is hydrogen and the other aromatic, the product may be either a monomer or a dimer; thus, phenyldibenzofulvene (IV) gives a dimeric dihydro product, while α-naphthyldibenzofulvene (V) yields a monomeric one.

IV
Phenyldibenzofulvene

$$C=CH \longrightarrow CH-CH_2$$

V
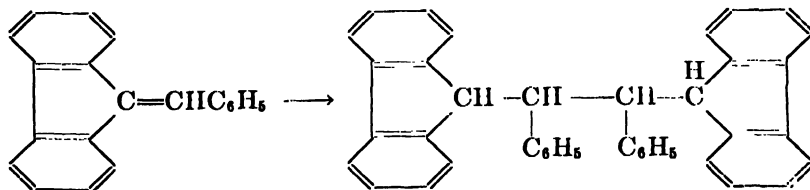
α-Naphthyldibenzofulvene
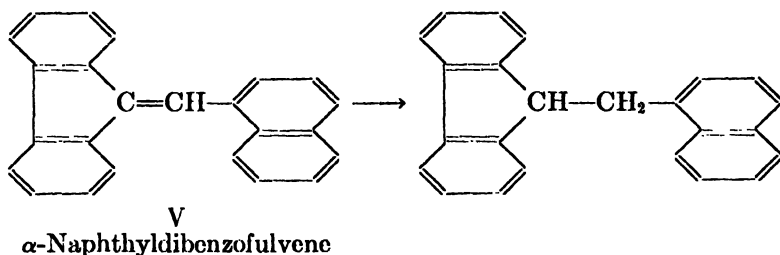
With the dibenzofulvenes (III) reduction by means of alkali metals in inert media followed by hydrolysis always occurs in the 1,2-position, at the external double bond, but the monobenzofulvenes (II) may yield either the 1,2- or the 1,4-reduction product, or both. Blum-Bergmann (39) has shown that reduction of triphenylbenzofulvene (VI) in this way gives both possible dihydro derivatives,

$$\begin{array}{ccc} CC_6H_5 & CC_6H_5 & CHC_6H_5 \\ \| & \| & \| \\ CH & CH & CH \\ C & CH & C \\ \| & | & \| \\ C(C_6H_5)_2 & CH(C_6H_5)_2 & CH(C_6H_5)_2 \end{array}$$

VI

Triphenylbenzofulvene
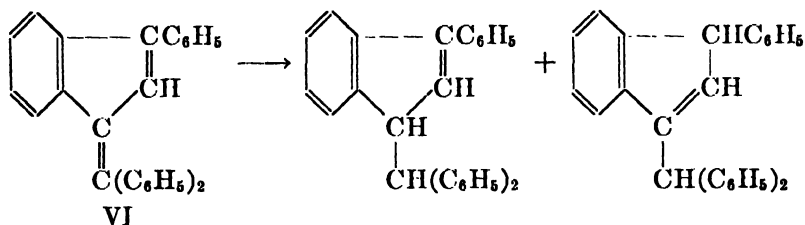
and diphenylbenzofulvene is converted to the 1,4-dihydro compound (39, 265).

Sodium and alcohol will also bring about the reduction of the fulvenes and their benzo analogs, regardless of the nature of the R groups. The reduction in some cases occurs in the 1,4-positions, as with dimethylbenzofulvene (300), and in other cases in the 1,2-positions, as with all the dibenzofulvenes (300) and with triphenylbenzofulvene (39).

Thiele and his students (35, 298, 299, 300, 341) and Sieglitz and Jassoy (281) have shown that the fulvenes, benzofulvenes, and dibenzofulvenes which contain at least one aryl or carboxyl group linked to the methylene carbon atom are reducible by aluminum amalgam in moist ether. When both the R groups are alkyl, this reagent does not bring about reduction (300). In the case of the dibenzofulvenes (III), reduction always occurs in the 1,2-positions (281, 299). With monobenzofulvenes (II) Thiele (298) originally considered that reduction always occurred in the 1,4-positions, to form indene derivatives,

$$\begin{array}{ccc} CH & CH_2 \\ \| & | \\ CH & CH \\ C & \longrightarrow & C \\ \| & | \\ CHC_6H_5 & CH_2C_6H_5 \end{array}$$
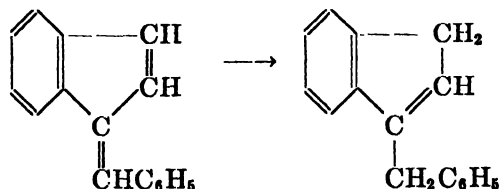
for the products of the reduction would condense with aldehydes to give substituted benzofulvenes. Wuest (341) showed, however, that the double bonds in

the reduction products are very labile, and condensation might well be preceded by rearrangement. As evidence that the reduction of benzofulvenes by aluminum amalgam is more complicated than Thiele considered it to be, Wuest cited the fact that the two isomers VII and VIII on reduction yielded the same mixture of two dihydro derivatives.
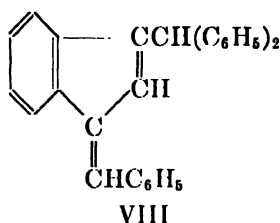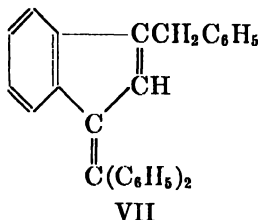
Two cases of reduction of hydrocarbons with open-chain crossed conjugated systems have been reported (265). In both cases addition to the double bond which was doubly conjugated occurred; in the case where one of the ethylenic carbon atoms was linked to two aryl groups, reduction without dimerization took place; in the other case, where no aryl groups were present, dimeric reduction occurred.

Table 6 gives a summary of the chemical reduction of compounds containing crossed conjugated systems.

4. Reduction of hydrocarbons with cumulated double bonds: allenes

Very few members of this class have been reduced; those that have, have been aryl substituted (see table 7). Tetraphenylallene, with two cumulated double bonds, is surprisingly inert to certain reducing agents. Vorländer and Weinstein (317) found that it is scarcely attacked by zinc and acetic acid or by sodium or aluminum amalgam, but that it is reduced by sodium and alcohol to the saturated compound, and by hydriodic acid and phosphorus to tetraphenylpropene. As the number of double bonds in the chain increases, however, this inertness disappears. Tetraphenylbutatriene (46a) is reduced by sodium in amyl alcohol to the saturated compound, and is readily attacked by zinc in the presence of hydrogen ion (46a, 176), in this case forming tetraphenylbutadiene. Tetraphenylpentatetraene is likewise rapidly reduced by zinc in the presence of acid (but not in its absence) (176).

Tetraphenylallene adds both lithium and sodium, but the hydrolysis products are not the same. Schlenk and Bergmann (265a) formulated the two reactions as follows:
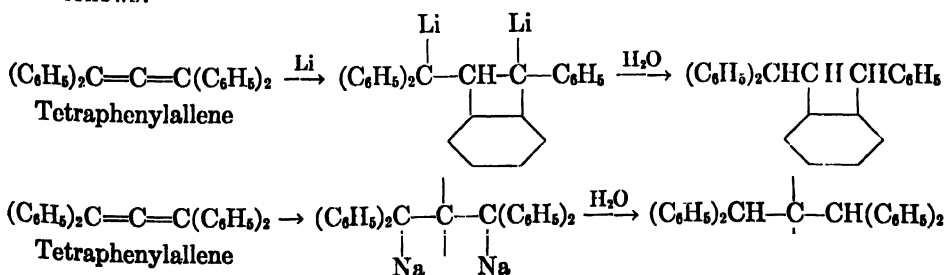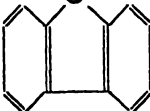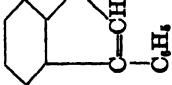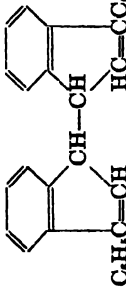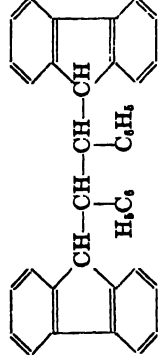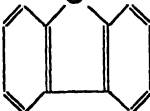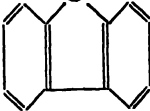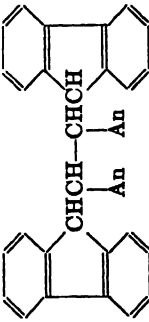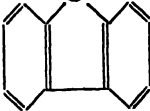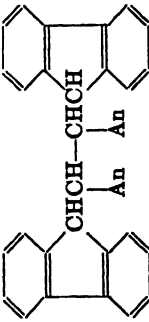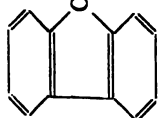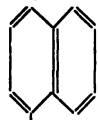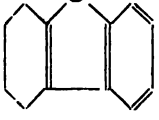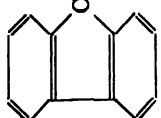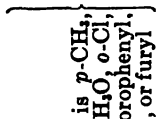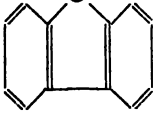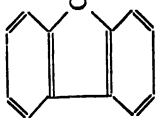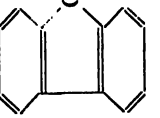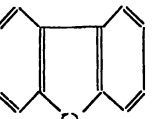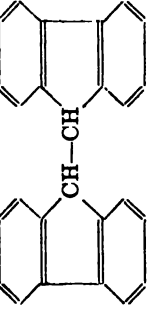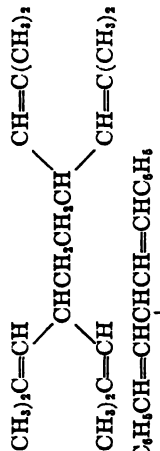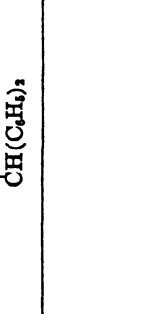
TABLE 6
Reduction of hydrocarbons with crossed conjugated systems

COMPOUND REDUCED	REDUCING AGENTS AND CONDITIONS	PRODUCTS	REFERENCES
CH=CH—C(CH₃)₂ / CH=CH—	Na (Li), ether	$\left[\text{CH=CH} \atop \text{CH=CH} \right]_2$ CH—C(CH₃)₂—	(265)
$\underset{R_2}{\overset{R_1}{\diagdown}}C{=}C\diagup$ where R₁ = R₂ = C₂H₅, R = CH₃, and R₂ = C₂H₅	Al amalgam	No reduction	(299a)
	Al amalgam	No reduction	(299a)
CH=CH—C(C₂H₅)₂ / CH=CH—	Na (Li), ether	CH=CH—CHCH(C₆H₅)₂ / CH=CH—	(265)
C=CHC₆H₄OCH₃(p)	Al amalgam	CH=CH—CHCH₂C₆H₄OCH₃ / CH=CH—	(299a)
(benzo) C=C(C₆H₅)₂ / CH=CH	Na (Li), ether	C—CH(C₆H₅)₂ / CH₂CH	(29, 265)
	Al amalgam		(300)
(benzo) C=CHY, where Y is phenyl, carboxyl, p-CH₃, p-CH₃O, p-Cl, and p-isopropylphenyl, or furyl / CH=CH	Al amalgam	C—CH₂Y / CH₂CH	(298)

(265)
(300)

(300)

(300)

(208)

(39)

Polymer
No reduction

and

Na, ether
Al amalgam

Na, alcohol

Al amalgam

Al amalgam

Na, ether

TABLE 6—*Concluded*

COMPOUND REDUCED	REDUCING AGENTS AND CONDITIONS	PRODUCTS	REFERENCES
	Na, alcohol	$CHCH(C_6H_5)_2$ (cyclohexyl ring with $C=CH$, C_6H_5)	(39)
(fluorene)$C=CHC_6H_5$	Na, ether	$CH-CH$ ... $HC=CC_6H_5$ and $CH-CH$ ... $C_6H_5C=CH$; $CH-CH-CH-CH$ with H_5C_6, C_6H_5	(265, 267a)
	Na, liquid NH_3	$CHCH_2C_6H_5$	(267a)
	Al amalgam		(298)
(fluorene)$C=CHC_6H_4OCH_3(p)$	Na, ether	$CHCH-CHCH$ with An, An	(267a)

Substrate	Reagent	Product	Reference
(naphthyl/anthracene) C=CH	Na, ether	(anthracene) CHCH₃	(267a)
(anthracene) C=CHAr, where Ar is p-CH₃, o-CH₃, p-CH₃O, o-Cl, m-Cl, p-chlorophenyl, β-naphthyl, or furyl	Al amalgam	(anthracene) CHCH₂Ar	(281), (298, 281)
(anthracene) C=CHCH₂CH₂C₆H₅	Al amalgam	No reduction	(298)
(dibenzofuran) C=C (anthracene)	Al amalgam	CH—CH (bridged)	(298)
$(CH_3)_2C=CHCCH=C(CH_3)_2$, with CH_2	Na, ether	$(CH_3)_2C=CH$ $CHCH_2CH_2CH$ $CH=C(CH_3)_2$	(265), (265)
$C_6H_5CH=CHCCH=CHC_6H_5$, $C(C_6H_5)_2$	Na, ether	$C_6H_5CH=CHCHCH=CHC_6H_5$ $CH(C_6H_5)_2$	(265)

It is more probable, however, that the compound obtained from the addition of sodium is tetraphenyl-1-propene.   Wooster and Ryan (339) have shown that the allene is reduced by sodium in liquid ammonia to tetraphenylpropane, and very possibly, in the light of Hückel's work (130), the reaction is a stepwise one, forming tetraphenylpropene as intermediate.

F. The stereochemical course of reduction

Much of the work on the reduction of acetylenes has centered around the geometrical configuration of the olefins obtained; until recently, this work was

TABLE 7

Reduction of hydrocarbons with cumulated double bonds

COMPOUND REDUCED	REDUCING AGENTS	PRODUCTS	REFERENCES
$(C_6H_5)_2C{=}C{=}C(C_6H_5)_2$	Na, ether	$(C_6H_5)_2CHCCH(C_6H_5)_2$?	(265a)
	Li, ether	$(C_6H_5)_2CHCH{-}{-}CHC_6H_5$	(265a)
	Na (K), liquid NH₃	$(C_6H_5)_2CHCH_2CH(C_6H_5)_2$	(339)
	Na, alcohol	$(C_6H_5)_2CHCH_2CH(C_6H_5)_2$	(317)
	Na amalgam	No reduction	(317)
	Al amalgam	No reduction	(317)
	Zn, acetic acid	No reduction	(317)
	HI, P, acetic acid	$(C_6H_5)_2CHCH{=}C(C_6H_5)_2$ and $(C_6H_5)_2CHCH_2CH(C_6H_5)_2$	(317)
$(C_6H_5)_2C{=}C{=}C{=}C(C_6H_5)_2$	Na, amyl alcohol	$(C_6H_5)_2CHCH_2CH_2CH(C_6H_5)_2$	(46a)
	Zn, acetic acid	$(C_6H_5)_2C{=}CHCH{=}C(C_6H_5)_2$	(46a)
$(C_6H_5)_2C{=}C{=}C{=}C{=}C(C_6H_5)_2$	Zn, H⁺	Rapid reduction	(176)
	Zn, H⁺	Rapid reduction	(176)
$C_6H_5C{=}C{=}C(CH_3)_2$ | CH₃	Na, alcohol	$C_6H_5CHCH{=}C(CH_3)_2$ | CH₃	(168b)

largely confined to tolane and the acetylenic acids.   Farkas and Farkas (90) have pointed out that, since the reduction of an unsaturated linkage in all probability occurs by a stepwise mechanism (see section II B), then the intermediate fragment formed by addition of the first proton has time to adjust its substituents to a position of minimum potential energy before the second stage of the addition occurs.   On this basis, the chemical reduction of disubstituted acetylenes should yield the *trans* olefins, and reduction of suitably substituted olefins should give the meso saturated compounds, since these are, in general, the more stable configurations.   On the other hand, if catalytic hydrogenation occurs by simultaneous addition of hydrogen to both carbon atoms of the unsaturated

linkage (90, 91, 92), the product should be the labile isomer, *cis* olefins from acetylenes, meso saturated compounds from *cis* olefins, and racemic saturated compounds from *trans* olefins. The information in the literature, in the main, confirms this theory, although there are exceptions, and the problem is complicated by the fact that much of the work has been done with compounds the reduction products of which can fairly readily be converted into their stereoisomers.

H   X   X   II   X
 \   / | \   /
  C   *cis* addition   C   *trans* addition   C
  ‖   ←――――――――――   〈 〉   ――――――――――→   ‖
  C   (catalytic)   C   (chemical)   C
 /   \ | /   \
H   X   X   X   II

    cis   *trans*

X   Y   X H Y   X   Y   X H Y   X H Y
 \   /   \ | /   \   /   \ | /   \ | /
  C   catalytic C   *trans*   C   *cis*   C   +   C
  ‖   ――――――→ | addition   ‖   addition | |
  C   or   C   ←――――――   C   ――――――→   C   C
 /   \ chemical / | \ (chemical)   /   \ (catalytic) / | \ / | \
X   Y   X II Y   Y   X   Y H X   Y H X

cis   meso   *trans*   racemic
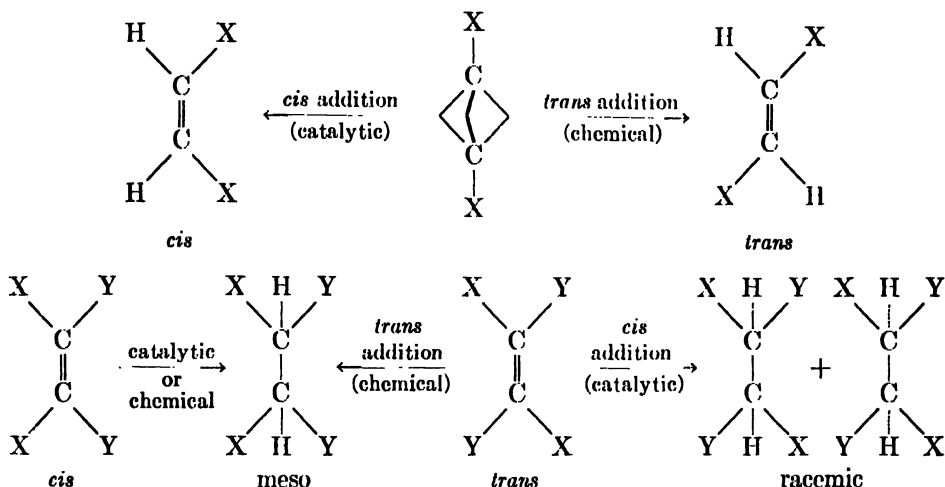
Gonzales (120) found that reduction of stearolic acid with zinc and acetic acid resulted in the *trans* olefinic acid, while catalytic hydrogenation yielded the *cis* form. Phenylpropiolic acid has been studied extensively. Aronstein (16) and Fischer (105) obtained cinnamic acid when zinc dust and acetic acid were used as the reducing agent, and Fischer considered this to be the primary reduction product, for *cis*-cinnamic acid is not converted to *trans*-cinnamic acid under the conditions used. Cinnamic acid is likewise formed when phenylpropiolic acid is treated with sodium in alcohol (16), although, since *cis*-cinnamic acid is easily converted to *trans*-cinnamic acid under these conditions, the latter may have been formed by rearrangement. Ott (226) considered that the stereochemical course of reduction of a triple bond is related to the reduction potential of the reducing agent; he postulated that reduction by the more noble metals should yield the *cis* forms, while the less noble metals should tend to yield the *trans* forms, and suggested that as the velocity of reduction is increased, a point should be reached where no olefin is obtained, the product being a mixture of the acetylene and the saturated compound. He tested this theory on phenylpropiolic acid, and reported the results given in table 8.

The chemical reduction of tolane can give either the *cis* or the *trans* form of stilbene, depending on the conditions. With sodium in methyl alcohol, or with zinc and acetic acid (291), the product is the ordinary (or *trans*) form of stilbene, but it should be pointed out that *cis*-stilbene is easily changed to the *trans* form by sodium (265a, 340a). *cis*-Stilbene is formed when tolane is reduced in aqueous medium with the zinc–copper couple (291).

Bourguel (43) reported that tetramethylbutyndiol is reduced to the *trans* olefinic glycol by sodium and alcohol; subsequent work by Zalkind (348) and by Johnson (147a) has shown, however, that the product is a polymorphic form of the original acetylenic glycol.

Less work has been done on the stereochemical course of the reduction of olefins than of acetylenes. Ott (227) found that *trans*-dimethylstilbene was reduced by sodium and alcohol to a stable equilibrium mixture of meso and racemic 2,3-diphenylbutanes. Since *cis*-dimethylstilbene is rapidly converted to the *trans* isomer by sodium, its reduction by alkali metals is really that of the *trans* form. Addition of alkali metals to the dimethylstilbenes, followed by hydrolysis, yields mesodiphenylbutane (265a).

Schlenk and Bergmann (265a) reported that addition of sodium and lithium to the *cis* and *trans* forms of stilbene took different stereochemical courses; more careful work by Wright (340a) has, however, shown that this is not true. Carbonation of the alkali-metal addition products yields a mixture of the meso- and

TABLE 8

Reduction of phenylpropiolic acid in ammoniacal ammonium chloride solution at 20°C. (226)

REDUCING AGENTS	PRODUCTS
Zn	Allocinnamic acid (10%)
Zn–Ag couple	Allocinnamic acid (24%)
Zn–Cu couple	Allocinnamic acid (37%)
Mn	Mainly allocinnamic acid, with 4 per cent of *trans* isomer
Mg, Ba amalgam, Na amalgam	Hydrocinnamic acid (50%) and phenylpropiolic acid (50%)
Cr^{++}	Mixture of *cis*- and *trans*-cinnamic acids
Ti^{+++}	Allocinnamic acid

dl-diphenylsuccinic acids, regardless of the alkali metal or stilbene used. The nature of the solvent exerts a marked effect on the relative amounts of the two acids formed, however.

The recent work of Campbell and Eby (56, 57) has given considerable support to the postulates of Farkas and Farkas (90), for they have shown that dialkylacetylenes are smoothly and easily reduced to *trans* olefins by sodium in liquid ammonia. Raman-spectra evidence indicates that the *trans* olefins so obtained are free from their *cis* isomers, and the configurations have been proved by freezing-point, dielectric-constant, and Raman-spectra data. Since *cis* olefins containing only alkyl groups are not converted to the *trans* forms by treatment with sodium (57, 363), the *trans* olefins obtained in this work must be the primary reduction products, and consequently, the reduction, in all probability, occurs by a stepwise mechanism. The *trans* isomers of all the straight-chain hexenes and octenes have been prepared in this way, as well as the *trans* forms of 2-methyl-3-octen-2-ol and 3,3-dimethyl-4-nonene. Reduction of dialkylacetylenes by lithium in liquid ammonia takes the same course, and yields the *trans* olefins (57).

The data on the stereochemical reduction of acetylenes and olefins are summarized in table 9.

The stereochemical configuration of the new double bond formed by 1,4-reduction of a conjugated diene varies with the nature of the reducing agent, and there seem to be no generalizations possible from the few cases that have been reported. Addition of sodium or lithium in an inert solvent, followed by hydrolysis, yields the *cis* form of 2-butene from butadiene (363), and *cis*-1,4-diphenyl-2-butene from 1,4-diphenylbutadiene (265a), but the *trans* olefin has been ob-

TABLE 9

Configuration of products obtained by chemical reduction of acetylenes and olefins

COMPOUND REDUCED	REDUCING AGENTS	PRODUCTS	REFERENCES
RC≡CR where R is ethyl, propyl, butyl.........	Na, liquid NH₃	*trans* RCH=CHR	(56, 57)
2-Hexyne..............	Na (Li), liquid NH₃	*trans*-2-Hexene	(56, 57)
2-Octyne.................	Na (Li), liquid NH₃	*trans*-2-Octene	(57)
3-Octyne.................	Na, liquid NH₃	*trans*-3-Octene	(56, 57)
3,3-Dimethyl-4-nonyne....	Na, liquid NH₃	*trans*-3,3-Dimethyl-4-nonene	(60)
2-Methyl-2-hydroxy-3-octyne	Na, liquid NH₃	*trans*-2-Methyl-2-hydroxy-3-octene	(57)
Stearolic acid............ CH₃(CH₂)₇C≡C(CH₂)₇-COOH	Zn, acetic acid	Elaidic acid (*trans*)	(120)
Behenolic acid............ CH₃(CH₂)₇C≡C(CH₂)₁₁-COOH	Zn, acetic acid	Brassidic acid (*trans*)	(120)
Diphenylacetylene.........	Na, methyl alcohol	*trans*-Stilbene	(16)
	Zn, acetic acid	*trans*-Stilbene	(16)
	Zn–Cu couple	*cis*-Stilbene	(291)
Phenylpropiolic acid.......	Na, alcohol	*trans*-Cinnamic acid	(16)
	Zn, acetic acid	*trans*-Cinnamic acid	(16, 105)
Dimethylstilbene.........	Na, ether	Diphenylethane (30% racemic, 70% meso)	(227)
	Na, alcohol	Diphenylethane (50% racemic, 50% meso)	(227)

tained in the same way from 1,1,4,4-tetraphenylbutadiene (38, 265a). Sodium amalgam causes the formation of *trans* olefins from di- and tetra-phenylbutadienes; it is possible that a stereochemical conversion ocurs here (265a). Reduction of 2,6-dimethyl-3,5-octadiene by sodium in liquid ammonia leads to a mixture of the *cis* and *trans* forms of 2,6-dimethyl-4-octene, with the *trans* form predominating. In this case, the configurations were established by Raman-spectra measurements (77). These data are summarized in table 10.

G. Reduction of aromatic hydrocarbons

A large amount of work has been done on the addition of alkali metals to aromatic hydrocarbons, and on the reduction of these hydrocarbons by alkali

metals in reactive solvents. Benzene and its simple homologs do not, in general, add alkali metals, and are not reduced by them. Most of the polynuclear hydrocarbons, on the other hand, do add alkali metals, especially lithium, and are reduced by these metals in alcohol or in liquid ammonia. Addition of lithium takes place with increasing ease in the order: naphthalene, phenanthrene, anthracene (265). Aromatic compounds are not usually attacked by sodium amalgam or aluminum amalgam (291), although anthracene is reduced by both (143, 291) and terephthalic acid is reduced by sodium amalgam (328). The addition of hydrogen or metals to polynuclear hydrocarbons has a strong tendency to occur in the 1,4-positions, and in this respect these compounds resemble the 1,4-diarylbutadienes. When the reaction is carried out in alcohol or liquid am-

TABLE 10

Configuration of olefins formed by chemical reduction of conjugated hydrocarbons

COMPOUND REDUCED	REDUCING AGENTS	PRODUCT	CONFIGURATION	REFERENCES
Butadiene.............	Na (Li), ether, ethylaniline	2-Butene	*cis*	(363)
1,4-Diphenylbutadiene . .	Na (Li), ether	1,4-Diphenyl-2-butene	*cis*	(265a)
	Na amalgam	1,4-Diphenyl-2-butene	*trans*	(265a)
1,1,4,4-Tetraphenylbutadiene.................	Na (Li), ether	1,1,4,4-Tetraphenyl-2-butene	*trans*	(265a)
	Na amalgam	1,1,4,4-Tetraphenyl-2-butene	*trans*	(265a)
5-Methyl-2,4-heptadiene...	Na, liquid NH$_3$	5-Methyl-3-heptene	*trans* mainly, some *cis*	(77)
2,3-Diphenylbutadiene....	Na, liquid NH$_3$	2,3-Diphenylbutane	meso	(12)

monia, a rearrangement of the primary reaction product is apt to occur, so that the product isolated is not always the 1,4-dihydro compound. Recent work by Scott (276, 277, 278, 318) and by Jeanncs and Adams (146) has shown that the addition of sodium, which in many cases is extremely slow in ether, is much more rapid in such solvents as the glycol ethers and dimethyl ether. The close parallel between the addition of alkali metals and reduction by these metals in reactive solvents gives strong support to Willstätter's theory (328),—as opposed to Baeyer's (23),—regarding the mechanism of this reduction (see section II B).

1. Reduction of naphthalene

Naphthalene adds sodium very slowly in diethyl ether, lithium more readily, and in both cases hydrolysis yields the 1,4-dihydro compound (265). Scott and Walker (278,318) have found that addition of sodium in ethylene glycol di-

methyl ether occurs more readily, and although but 1 gram-atom of sodium is taken up per mole of naphthalene, hydrolysis yields the 1,4-dihydro compound; possibly a complex of the type $C_{10}H_8Na_2 \cdot C_{10}H_8$ is formed.
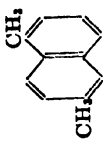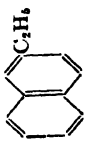
Naphthalene is easily reduced by sodium in liquid ammonia. Lebeau and Picon (183), who first studied this reaction, carried it out at room temperature, and obtained the 1,2,3,4-tetrahydronaphthalene and sodium amide. They considered that reduction was preceded by the formation of an organo-sodium compound, for at −10°C. and below, the solution had the red color of organo-sodium solutions, and by adding ethyl bromide to the colored solution they obtained an ethylated product. Subsequent workers have confirmed and amplified these results.

Wooster and Smith (340), in the course of a detailed study of this reaction, showed that the 'nascent'-hydrogen theory of Baeyer (23), proposed to explain such reduction, is untenable, for when naphthalene and sodium were allowed to react in liquid ammonia, titration showed that only four atoms of sodium reacted per molecule of naphthalene, regardless of the presence of excess sodium. These workers believed that a 1,2,3,4-tetrasodium derivative was formed, and that this was three-fourths ammonolyzed, even at low temperatures. More recent work of Hückel and Bretschneider (130) shows, however, that the reaction of sodium with naphthalene in liquid ammonia follows a stepwise course. At low temperatures (−75° to −60°C.) a 1,4-disodium naphthalene is formed (this is, of course, analogous to the 1,4-addition of sodium to 1,4-diphenylbutadiene). This disodium salt is stable at these low temperatures, but at higher temperatures it is ammonolyzed, yielding 1,4-dihydronaphthalene. At −33°C. this substance, in the presence of sodium amide, rearranges to the 1,2-dihydronaphthalene, which, since it is a 1-arylolefin, is reduced by sodium in liquid ammonia to tetralin.

Naphthalene

Tetralin
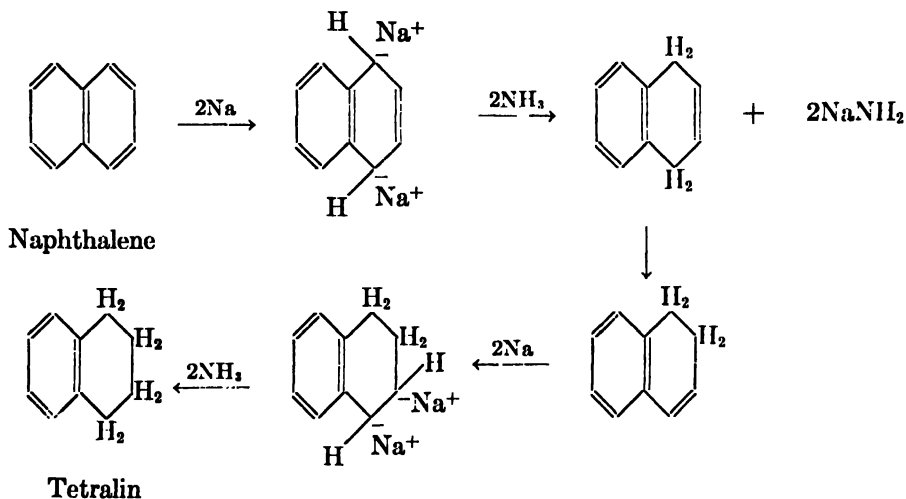
Since calcium in liquid ammonia reacts with naphthalene as does sodium (130), Hückel considers that the real mechanism of the reduction is the addition of

TABLE 11

Reduction of aromatic hydrocarbons by chemical reducing agents

COMPOUND REDUCED	REDUCING AGENTS AND CONDITIONS	PRODUCTS	REFERENCES
Naphthalene........	Na, ether	No addition	(265a)
	Li or K, ether	1,4-Dihydro	(265a)
	Na, glycol ether	1,4-Dihydro	(276, 278, 318)
	Na (Ca), liquid NH₃, −75°C.	1,4-Dihydro	(130)
	Na, liquid NH₃, −33°C.	1,2-Dihydro and 1,2,3,4-tetrahydro	(130, 340)
	Na, liquid NH₃, room temperature	1,2,3,4-Tetrahydro	(183)
	Na, ethyl alcohol	1,4-Dihydro	(25)
	Na, ethyl alcohol, solvent naphtha	1,2,3,4-Tetrahydro	(27)
	Ca, ethyl alcohol	1,4-Dihydro	(207)
	Na, amyl alcohol	1,2,3,4-Tetrahydro	(255)
	Na amalgam	No reduction	(291)
	Ca(NH₃)₆, room temperature	Tetralin and decalin	(157)
	Na, amyl alcohol	5,8-Dihydro	(209)
1,6-Dimethylnaphthalene..			
2-Ethylnaphthalene.......	Na, amyl alcohol	Mixture of dihydro products	(193)
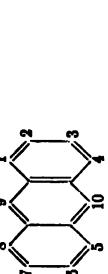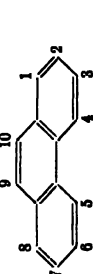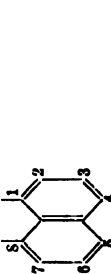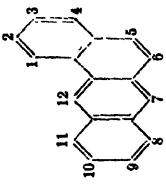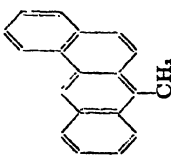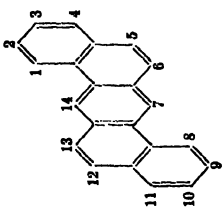
Anthracene..........	Na, ether	9,10-Dihydro	(264, 265a)
	Na, glycol ether	Disodium salt	(277)
	Na, liquid NH₃, −33°C. or room temperature	9,10-Dihydro	(184, 214, 323)
	Na (Ca), alcohol	9,10-Dihydro	(323, 207)
	Na, amyl alcohol	9,10-Dihydro	(26)
	Na amalgam, alcohol	9,10-Dihydro	(291)
	Na, Al, Mg amalgams	9,10-Dihydro	(143)
	HI + P, 160–170°C.	9,10-Dihydro	(201)
	220°C.	Hexahydro	
	250°C.	Perhydro	
9,10-Diphenylanthracene..........	Na (Li), ether	9,10-Dihydro	(265a)
	Na (K), liquid NH₃	9,10-Dihydro	(135)
	Na, amyl alcohol	9,10-Dihydro	(265)
Phenanthrene..........	Na, ether	Slow addition	(265a)
	Li, ether	9,10-Dihydro	(265a)
	Na (Li), glycol ether	9,10-Dihydro	(146)
	Na, liquid NH₃, −75°C.	With two sodium, incomplete reaction; with four sodium, a non-uniform product	(130)
	Na, liquid NH₃, room temperature	Tetrahydro, unproved structure	(184)
	Na, alcohol	9,10-Dihydro and 5,6,7,8-tetrahydro	(274)
	Na amalgam	No reduction	(291)
	Zn + Pd, HCl	Tetrahydro entirely	(49)
	HI + P, 200°C.	Tetrahydro	(122)
	240°C.	Octahydro	
Acenaphthene.......... H₂C—CH₂	Na, glycol ether	Disodium salt	(277)
	Na, liquid NH₃, room temperature	Tetrahydro, unproved structure	(184)
	Na, amyl alcohol	1,2,3,4-Tetrahydro	(26, 47)
	HI + P	Decahydro	(194)

TABLE 11—*Continued*

COMPOUND REDUCED	REDUCING AGENTS AND CONDITIONS	PRODUCTS	REFERENCES
1,2-Benzanthracene............	Na, ether Na, amyl alcohol	7,12-Dihydro 1,2,3,4,7,12-Hexahydro	(22, 103) (103)
7-Methylbenzanthracene........	Na, ether Na, amyl alcohol	7,12-Dihydro 1,2,3,4,7,12-Hexahydro	(103) (103)
Dibenzanthracene............	Na (Li), ether	7,14-Dihydro	(22)
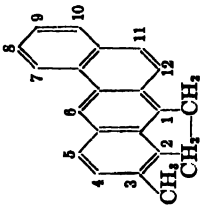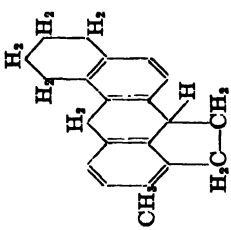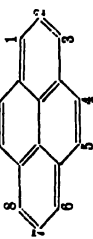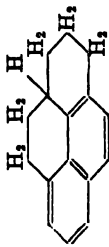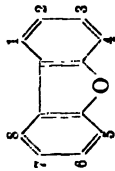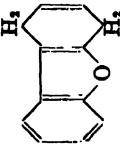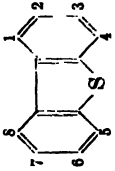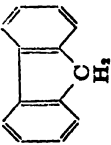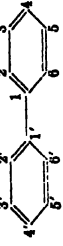
Compound	Reagent	Product	Ref.
3-Methylcholanthrene	Na (Li), ether; Na, amyl alcohol	Dihydro (meso), Hexahydro,	(22, 104)
Pyrene	Na (Li), ether; Na, amyl alcohol	Recovered pyrene: 1,2,3,6,7,8- Two hexahydro: and	(30)(66)
Dibenzofuran	Na, liquid NH₃	1,4-Dihydro,	(112)
Dibenzothiophene	Na, liquid NH₃	1,4-Dihydro	(112)

TABLE 11—*Concluded*

COMPOUND REDUCED	REDUCING AGENTS AND CONDITIONS	PRODUCTS	REFERENCES
Fluorene........	Na, liquid NH₃	Chiefly substitution	(184)
Benzene........	Na, liquid NH₃	No reaction	(184)
	Na, liquid NH₃, CH₃OH	1,4-Cyclohexadiene	(336)
	Ca(NH₃)₆, room temperature	Cyclohexene	(154, 157)
	Sr, Ba, Li-NH₃ complexes	Cyclohexene, in poorer yields	(155)
	HI + P	Not readily attacked	(24)
Toluene........	Na, liquid NH₃	No reaction	(184)
	Na, liquid NH₃, H₂O or CH₃OH	1,4-Dihydro	(336, 338)
	HI + P, 310°C.	Dihydro (?)	(24)
	Ca(NH₃)₆	1-Methyl-1-cyclohexene	(154, 157)
Xylenes:			
meta.	Ca(NH₃)₆	1,3-Dimethyl-3-cyclohexene	(154)
	HI + P, 310°C.	Tetrahydroxylene	(24)
para.	Ca(NH₃)₆	1,4-Dimethyl-3-cyclohexene	(154)
ortho.	Ca(NH₃)₆	Non-homogeneous product	(154)
Mesitylene........	Ca(NH₃)₆	Difficult to reduce; gives 1,3,5-trimethyl-1-cyclohexene	(154)
Biphenyl........	HI + P, 350°C.	Hexahydro	(24)
	Na, ether	Addition very slow	(265a)
	Li, ether	Dihydro, 1,4- (?)	(265a)
	Na, liquid NH₃, −65°C.	1-Phenyl-1-cyclohexene	(130)
	Na, liquid NH₃, room temperature	Tetrahydro	(184)
Terphenyl........	Na, amyl alcohol	Tetrahydro	(26)
	Na, ether	1′,4′-Dihydro (?)	(265a)
	Na, liquid NH₃	1′,2′-Dihydro and C₁₈H₁₄	(130)
Terephthalic acid........	Na amalgam, pH 10–12	1,4-Dihydro	(328)
	Na amalgam, pH 9	*p*-Toluic acid	(328)

electrons to the 1,4-positions of the naphthalene, to form a doubly negative ion (see section .II B).

The tendency of naphthalene to react similarly to 1,4-diphenylbutadiene is further exemplified by its reduction with sodium and ethyl alcohol, which yields the 1,4-dihydro derivative (25). If amyl alcohol is used instead of ethyl, the 1,4-dihydronaphthalene is the initial product, but the presence of alkali and the higher temperature causes this to rearrange to the 1,2-dihydro isomer, which is further reduced to tetralin (255).

The chemical reduction of naphthalene homologs has not been studied to any great extent. Mayer and Schulte (209) report the reduction of 1,6-dimethyl-naphthalene with sodium and amyl alcohol as forming the 5,8-dihydro derivative by 1,4-reduction. Under the same conditions, 2-ethylnaphthalene forms a mixture of dihydro compounds (193).

Acenaphthene adds sodium in ethylene glycol dimethyl ether; the structure of the product has not been established, but presumably it is the 1,4-compound (277). Reduction of acenaphthene by sodium in liquid ammonia (184) and by sodium and amyl alcohol (47) is similar to that of naphthalene; it yields the tetralin.

2. Reduction of anthracene

This hydrocarbon is more easily reduced by alkali metals than are naphthalene and phenanthrene, and in reduction, as in other reactions, it is attacked in the 9,10-positions; the 9,10-dihydroanthracene, containing as it does two independent benzene rings, is not further attacked by chemical reducing agents.

Anthracene   9,10-Dihydroanthracene
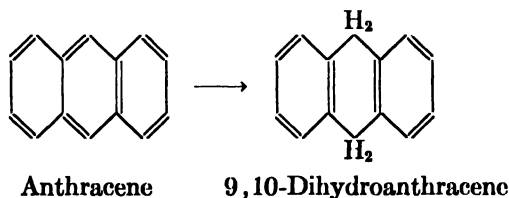
Anthracene has been reduced to the 9,10-dihydro derivative by the addition of sodium or lithium in ethylene glycol ethers (277) or in diethyl ether (264,265), followed by hydrolysis; by sodium or potassium in liquid ammonia (184,214); and by sodium or calcium and alcohol (207,323). Even the use of sodium and amyl alcohol does not carry the reduction beyond the dihydro stage (26,122). Unlike many of the other polynuclear hydrocarbons, anthracene can be reduced by sodium amalgam (122,143) and by aluminum and magnesium amalgams (143).

9,10-Diphenylanthracene, like anthracene, is reduced in the 9,10-positions by sodium and alcohol and by sodium in liquid ammonia (135); on treatment with sodium or lithium in ether, it forms the 9,10-dimetallic salt (265a). In connection with the stereochemical course of chemical reductions, it is interesting to note that hydrolysis of the disodium salt produces a 9,10-dihydro-9,10-diphenyl-anthracene which is a stereoisomer of the one obtained by reduction with sodium and amyl alcohol (265a).

3. Reduction of phenanthrene

Phenanthrene is less easily attacked by alkali metals than is anthracene: in diethyl ether it adds lithium readily, but sodium only slowly (265a); if, however, the addition of sodium is carried out in ethylene glycol dimethyl ether, it takes place much more rapidly (146). The first attack of alkali metals on phenanthrene is in the 9,10-positions, for hydrolysis of the disodium salt yields 9,10-dihydrophenanthrene (146). In contrast to anthracene, however, the dihydro derivative of phenanthrene can be reduced further by alkali metals. Thus, reduction by sodium and ethyl alcohol converts phenanthrene to the 9,10-dihydro compound, but if amyl alcohol is used instead, some 5,6,7,8-tetrahydrophenanthrene is also obtained (274). The formation of this tetrahydro derivative from the dihydro involves a shift of double bonds; a similar shift occurs during the catalytic hydrogenation of phenanthrene (274).

Phenanthrene   9,10-Dihydro-   5,6,7,8-Tetrahydro-
                       phenanthrene   phenanthrene
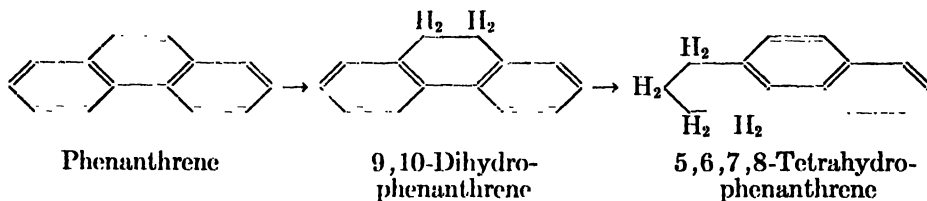
When phenanthrene is treated with two equivalents of sodium in liquid ammonia, the reaction is incomplete, although some 9,10-dihydrophenanthrene is formed. If four equivalents of sodium are used, a non-uniform tetrahydro product is obtained (130). Unlike anthracene, phenanthrene is not attacked by sodium amalgam (122).

In 1,2-benzanthracene (I, R=H), its 5-methyl derivative (I, R=CH₃), in 3-methylcholanthrene (II), and in 1,2,5,6-dibenzanthracene (III), both anthracene and phenanthrene ring systems are present. Since anthracene is more easily reduced by alkali metals than is phenanthrene, it might be predicted that the anthracene ring system in these compounds would be attacked first by such reducing agents, and this is, in fact, the case. Addition of sodium or lithium in an inert solvent, followed by hydrolysis, yields the meso dihydro compound. When sodium and amyl alcohol are used, the reduction proceeds farther, and the terminal ring of the phenanthrene system is also reduced, so that a hexahydro derivative is formed. These results are in contrast to those obtained by catalytic hydrogenation, in which the terminal ring of the anthracene system is attacked.

I

(22, 103)

3-Methylcholanthrene

(22, 104)

(22)

III
1,2,5,6-Dibenzanthracene
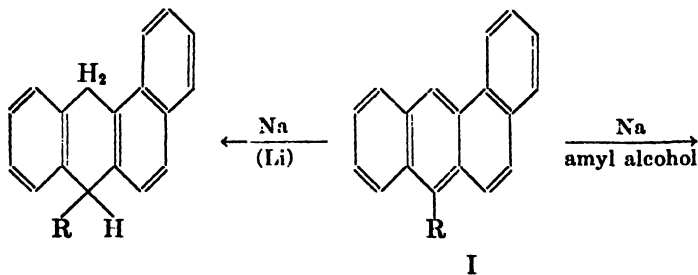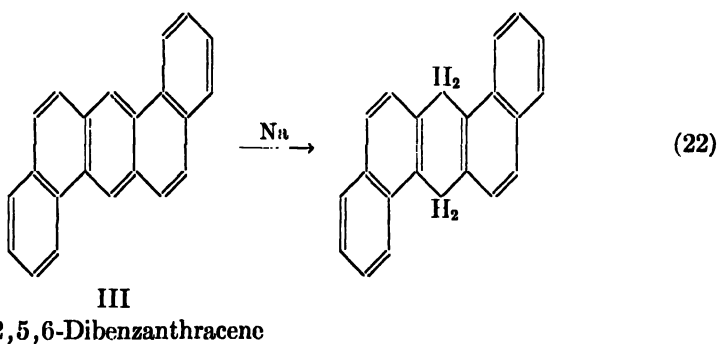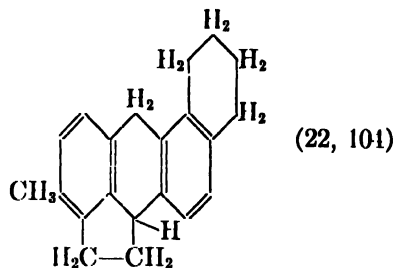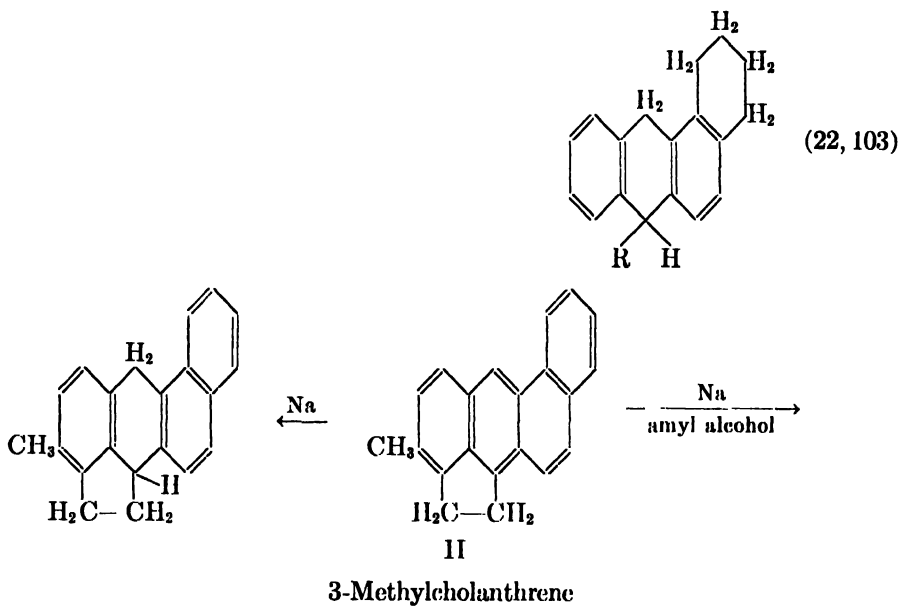
Pyrene in ether solution forms a dilithium salt (30), but hydrolysis of this salt regenerates the original compound, indicating that the dihydro compound is unstable and autoöxidizable. It, therefore, cannot be the dihydro compound (IV), which would be formed if the addition took the same course as it does in phenanthrene, for compound IV has been obtained by catalytic hydrogenation of pyrene, and it is stable. As in the case of phenanthrene, reduction of pyrene by

sodium and amyl alcohol leads to the addition of six hydrogen atoms, and a mixture of two hexahydropyrenes is obtained (66).

IV

Pyrene   Hexahydropyrene   +

Hexahydropyrene
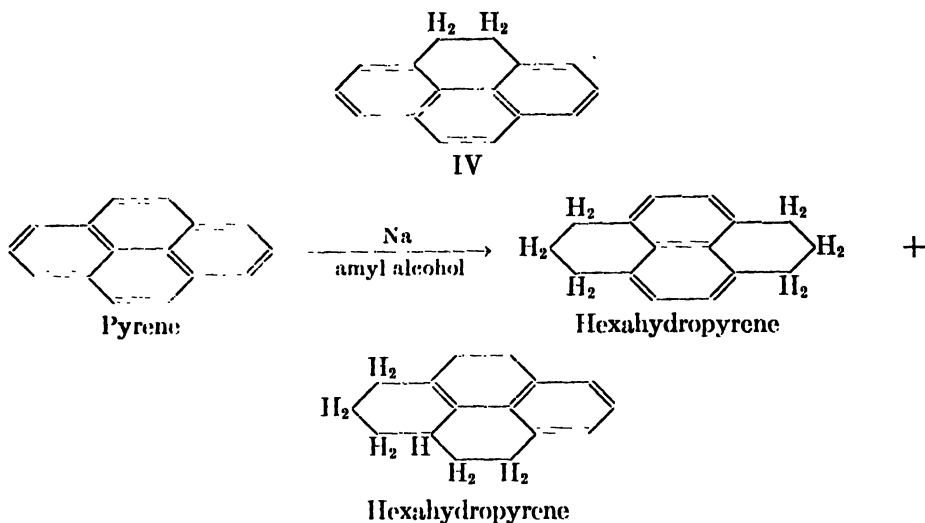
4. Reduction of benzene and its derivatives

Although benzene and the alkylbenzenes do not, in general, react with alkali metals, the aryl-substituted ones do. Sodium reacts very slowly with biphenyl in ether solution, lithium more readily, to yield a salt to which Schlenk and Bergmann (265) assigned the 1,4-structure.
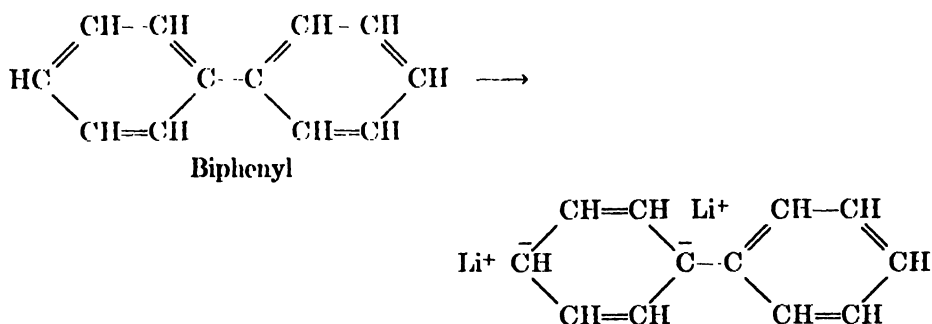
Biphenyl

Hückel and Bretschneider (130), however, found that biphenyl reacts with sodium in liquid ammonia at low temperatures to give a tetrahydro compound, and they formulated the reaction as involving first 3,4-addition, followed by 1,4-addition to the phenylcyclohexadiene formed as intermediate.
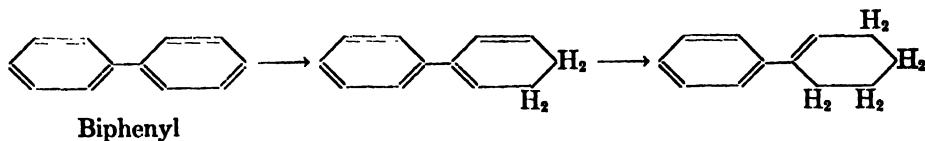
Biphenyl

Terphenyl, on treatment with sodium in ether, yields a disodium salt, which Schlenk and Bergmann (265) considered resulted from 1,4-addition to the central benzene ring.
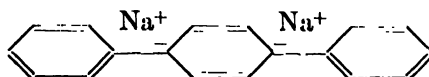
Hückel and Bretschneider (130), on the other hand, obtained a dihydroterphenyl from the action of sodium in liquid ammonia, to which they assigned the following structure, since the compound contained a conjugated system:
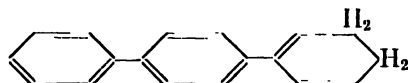
There are two exceptions to the statement that benzene and toluene are not attacked by alkali metals. No metal salt is obtained when these hydrocarbons are treated with sodium or lithium in inert solvents, and no reduction takes place when they are treated with sodium and alcohol, or sodium in liquid ammonia under ordinary conditions. Wooster and Godfrey (338) have, however, found that when a solution of toluene and sodium in liquid ammonia is treated with water, far less than the theoretical amount of hydrogen is evolved, and a highly unsaturated compound is obtained. This may be a true case of reduction by 'nascent' hydrogen, since no reaction occurs between the sodium and the toluene in the absence of water. A recent patent issued to Wooster (336), in extension of this work, describes the preparation of 1,4-dihydrobenzene and 1,4-dihydrotoluene by treating the hydrocarbons with sodium in liquid ammonia in the presence of a hydrolytic agent such as methyl alcohol.

Substitution of one or more of the hydrogen atoms of the benzene ring by hydroxyl or carboxyl groups renders the products more susceptible to reduction by chemical agents; although a detailed discussion of these cases is beyond the scope of this article, mention should be made of the results of Willstätter and his students on the reduction of terephthalic acid by pure sodium amalgam (328). The course of this reduction is markedly affected by the hydrogen-ion concentration of the medium; at a pH of 10–12, nuclear reduction occurs, and a mixture of the $\Delta^{2,5}$-dihydro and Δ^2-tetrahydro acids is obtained.

Terephthalic acid
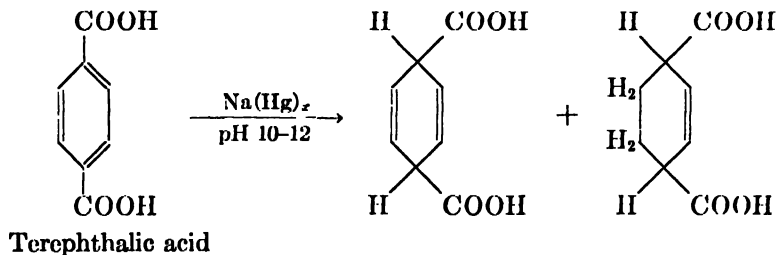
When, on the other hand, the pH is maintained at 9 9.8 by the use of buffers, nuclear reduction ceases to be the main reaction, and instead, one of the carboxyl groups is attacked, with the formation of p-toluic acid.

$$\text{Terephthalic acid} \xrightarrow[\text{pH } 9\text{–}9.8]{\text{Na(Hg)}_x} \text{p-Toluic acid}$$

Terephthalic acid p-Toluic acid
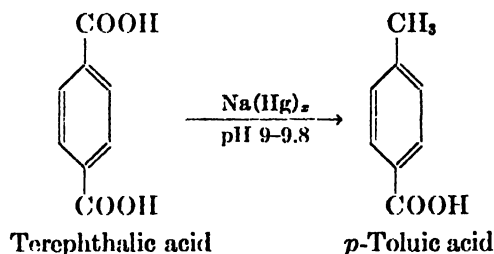
Similar results have been obtained with benzoic acid (210).   Reduction by sodium amalgam in alkaline solution yields a tetrahydro acid, whereas reduction in acid medium forms benzyl alcohol.

$$\xleftarrow[\text{base}]{\text{Na(Hg)}_x} \quad \text{Benzoic acid} \quad \xrightarrow[\text{acid}]{\text{Na(Hg)}_x} \text{Benzyl alcohol}$$

Benzoic acid   Benzyl alcohol
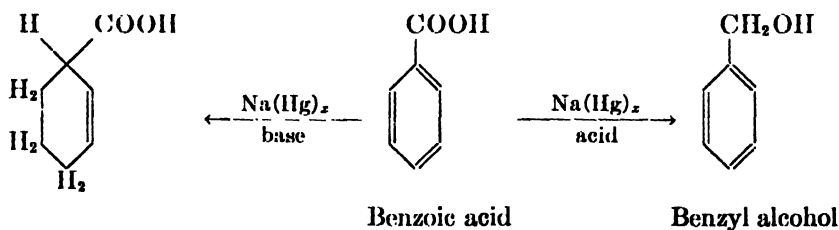
Calcium ammonia, $Ca(NH_3)_6$, made by passing ammonia vapors over metallic calcium, is a powerful reducing agent for aromatic compounds.   It will reduce benzene and its homologs at room temperatures to cyclohexene derivatives, in yields as high as 90 per cent.   With alkylbenzenes, the double bond of the cyclo-hexene is linked to the same carbon atom as the alkyl group (154, 157).   The ammonia complexes of lithium, strontium, and barium can also be used (155), but they are much less effective.

Hydriodic acid and red phosphorus may be used to reduce most aromatic hydrocarbons; frequently a mixture of products is obtained, and the reduction can be made complete if a sufficiently high temperature is used.   Other methods of reduction are generally preferable.

The aromatic hydrocarbons are not, as a rule, reduced by zinc and acid, but Breteau (49) has reported the reduction of phenanthrene with zinc activated by palladium chloride, in hydrochloric acid solution.   The tetrahydro derivative was obtained, regardless of the amount of reducing agent used, and no dihydro- or hexahydro-phenanthrene could be isolated.   This may possibly be a case of catalytic hydrogenation, in which the palladium functioned as catalyst and the hydrogen was generated by interaction of the zinc and hydrochloric acid.

II. Reduction of α,β-unsaturated carbonyl compounds

The presence of a carbonyl group adjacent to the carbon–carbon unsaturation activates the latter, so that reduction by chemical agents occurs readily in most instances.   Since these reactions are well known, a detailed discussion will not be given here, but certain points of especial interest will be covered.

Sodium and alcohol, or sodium amalgam, will reduce practically all of these compounds; zinc and acetic acid or the zinc–copper couple will bring about the reduction of unsaturated aldehydes and ketones, acetylenic acids, and unsat-

urated dicarboxylic acids; and the soluble reducing agents, such as titanium trichloride and chromous chloride, will reduce many of the compounds in this group, but are without action on aliphatic α,β-ethylenic acids (65,150).

While the net result of the reaction is usually addition of hydrogen to the carbon-carbon unsaturation, it is probable that the reaction proceeds largely, if not entirely, by 1,4-addition to the C=C—C=O system, since the oxygen atom provides a ready seat for a proton:

$$RCH=CH-C=O \longrightarrow R\overset{*}{C}H-CH=C-O: \xrightarrow{2e + H^+} R\overset{..}{C}H-CH=C-OH$$

with R' substituents below.

$$\xrightarrow{H^+} R\overset{H}{C}H-CH=C-OH \longrightarrow RCH_2CH_2C=O$$

with R' substituents below.
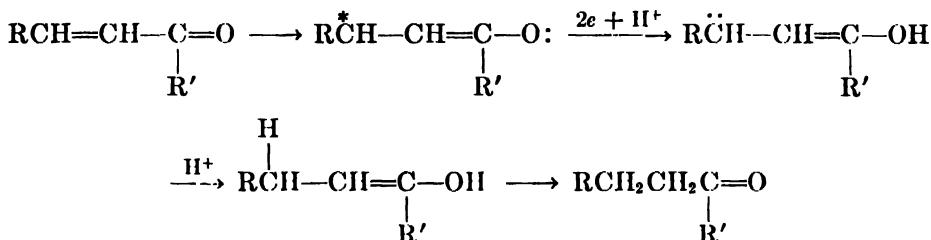
Recent work of Kohler and Thompson (170) on the reduction of β-phenylbenzalacetomesitylene (I) has shown that the initial reduction product, when zinc and acetic acid are used, is the enol (II), which, in this case, is fairly stable and can be converted to its peroxide before it ketonizes.

$$(CH_3)_3C_6H_3C-CH=C(C_6H_5)_2 \xrightarrow{\quad Zn + CH_3COOH \quad}$$

$$\overset{\|}{O}$$

I

β-Phenylbenzalacetomesitylene

$$(CH_3)_3C_6H_3C=CH-CH(C_6H_5)_2$$

$$\overset{|}{OH}$$
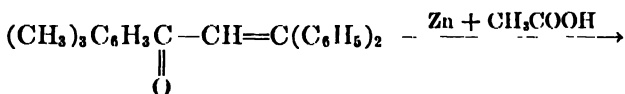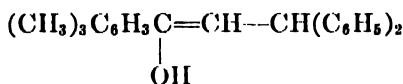
II

The reduction of unsaturated 1,4-diketones has been shown to take place by 1,6-addition of hydrogen, for furan derivatives are obtained which could not have arisen, under the conditions used, from the saturated diketone (202, 203).

$$C_6H_5\overset{O}{\overset{\|}{C}}-CH=C-\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{\quad Zn + CH_3COOH \quad} C_6H_5\overset{OH}{\overset{|}{C}}=CH-C=\overset{OH}{\overset{|}{C}}C_6H_5 \longrightarrow$$

with C_6H_5 substituents below.

$$\begin{array}{c} HC\text{————}CC_6H_5 \\ C_6H_5C\quad\quad CC_6H_5 \\ \diagdown\,O\,\diagup \end{array}$$
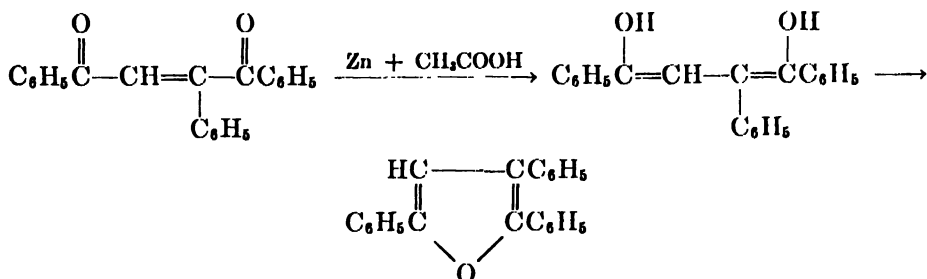
The mechanism of conjugate addition, followed by ketonization, was proposed by Conant and Cutter (65a) to correlate the reversible reduction of quinones by soluble reducing agents with the irreversible reduction of aliphatic unsaturated

keto acids and dicarboxylic acids. The fact that succinic and maleic acids do not form a reversible oxidation–reduction system is attributed to the practical irreversibility of the ketonization step. Conant and his coworkers (63,65,65a) were able, however, to determine the apparent reduction potential of a series of unsaturated acids and ketones, and showed that the reduction of these substances is dependent on the potential of the reducing agent, and not on the specific chemical properties thereof.

With α,β-unsaturated ketones there is a strong tendency for dimeric reduction products to be formed, especially with aluminum amalgam and soluble reducing agents. The mechanism of this reaction is probably similar to that postulated earlier for the dimeric reduction of certain arylolefins; that is, the molecule acquires but one electron instead of two from the reducing agent, and the free radical so formed stabilizes itself by dimerization. Two free radicals are possible: one with the odd electron attached to the carbon atom of the carbonyl group, the other with it attached to the terminal carbon atom of the C=C—C=O chain; in the case of α,β-unsaturated ketones the latter seems to be the one usually formed, whereas with certain unsaturated aldehydes dimerization occurs through the carbon of the carbonyl group (65).

$$C_6H_5CH=CH-\underset{\underset{O}{\|}}{C}-C_6H_5 \longrightarrow C_6H_5\overset{*}{C}H-CH=\underset{\underset{O:}{|}}{C}-C_6H_5 \xrightarrow{1e}$$

$$C_6H_5\overset{\bullet}{C}H \quad CH=\underset{\underset{O:}{|}}{C}-C_6H_5 \longrightarrow \begin{array}{c} C_6H_5CH-CH=\overset{\overset{O:}{|}}{C}-C_6H_5 \\ | \\ C_6H_5CH-CH=\underset{\underset{O:}{|}}{C}-C_6H_5 \end{array} \xrightarrow{2H^+}$$

$$\begin{array}{c} O \\ \| \\ C_6H_5CHCHCC_6H_5 \\ | \\ C_6H_5CHCHCC_6H_5 \\ \| \\ O \end{array}$$

$$CH_2=CH-CH=O \xrightarrow[1e]{H^+} CH_2=CHCHOH \longrightarrow \begin{array}{c} CH_2=CHCHOH \\ | \\ CH_2=CHCHOH \end{array}$$
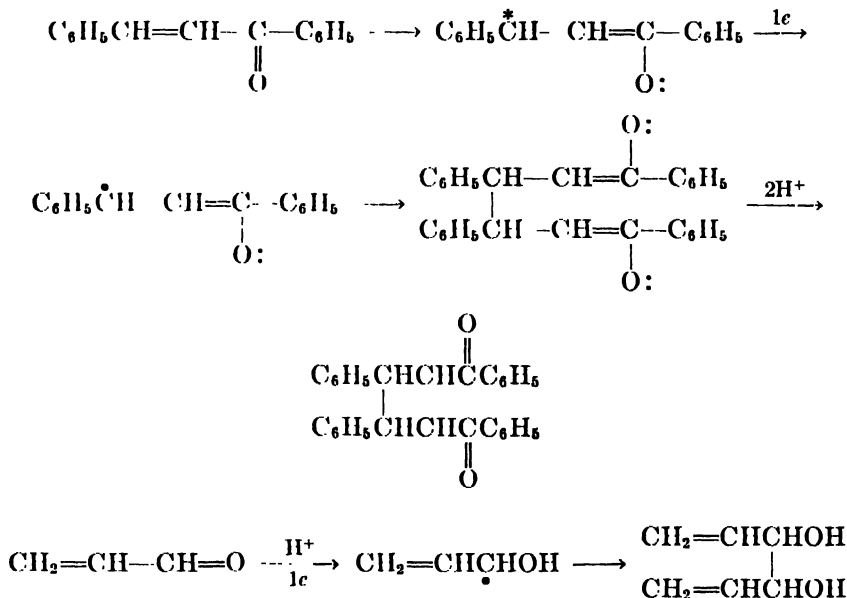
Since α,β-unsaturated aldehydes and ketones, unlike maleic acid and unsaturated keto acids which contain the system O=C—C=C—C=O, are only reduced by soluble reducing salts (vanadous chloride, chromous chloride, etc.) in acid solution, and the ease of the reduction is a function of the hydrogen-ion concentration, Conant and Cutter (65) have postulated that the compounds themselves are incapable of acquiring an electron from the reducing salt (although they can from a metal surface), but that they form a halochromic salt in the acid solution, which is capable of acquiring electrons from the reducing agent.

I. Reduction of polyene acids, aldehydes, and ketones

Since in these molecules the ethylenic bond is activated by conjugation with a carbonyl group and also with another ethylenic group, reduction by chemical means is very easy, and these substances may be reduced by aluminum amalgam as well as by the stronger reducing agents. Because the compounds are, with few exceptions, unsymmetrical, the course of the reduction is complex. The picture is further complicated by the fact that the products of partial reduction may be rearranged into one another by heat and base, and analytical methods are in many cases tedious and inexact. It is not surprising, therefore, that discrepancies exist in the literature as to the course of reduction.

If the theory first proposed by Burton and Ingold (54) is applied to a compound containing the group RC=C—C=C—C=O, and the assumption is made that the reaction is initiated at the oxygen atom, then, when addition of one hydrogen ion and two electrons has occurred, two intermediate ions are possible:

$$\overset{6}{RC}=\overset{5}{C}-\overset{4}{C}=\overset{3}{C}-\overset{2}{C}=\overset{1}{O} \xrightarrow[2e]{H^{\cdot}} RC-C=C-C=C-OH \xrightarrow{H^{+}} RCH-C=C-CH-C=O$$

$$\text{I} \qquad\qquad\qquad\qquad\qquad\qquad \text{III}$$

$$\Updownarrow$$

$$RC=C-C-C=C-OH \xrightarrow{H^{+}} RC=C-CH-CH-C=O$$

$$\text{II} \qquad\qquad\qquad\qquad\qquad \text{IV}$$

The proportions of the products III and IV, formed by addition of a second hydrogen ion and ketonization, will depend on the way the tautomerism between the ions I and II is displaced, which will, in turn, depend on the nature of the substituents and on the experimental conditions.

If R is an electron-attracting group, and there are no other such groups in the system, then ion I should be the more stable, and the dihydro product should have structure III. This is experimentally true: cinnamalacetic acid (R = C_6H_5) (19,54,257), cinnamalmalonic acid (19,54), and similar compounds are all reduced by chemical reducing agents to the β,γ-unsaturated acids. Muconic acid (R = COOH) is also reduced to the β,γ-unsaturated acid (54,86), but here probably the reaction involves addition of hydrogen to the two carbonyl groups at the ends of the conjugated chain.

When R is alkyl or hydrogen, a mixture of dihydro products is usually obtained. The relative amounts of forms III and IV depend on the other substituents. In the case of β-phenylsorbic acid, $CH_3CH=CHC(C_6H_5)=CHCOOH$, it might be expected that ion II would predominate, owing to the electron-attracting nature of the phenyl group, and that, therefore, the dihydro product would have structure IV. Kuhn and Hoffer (175), however, found that about 70 per cent of terminal addition occurred with sodium amalgam, and that only about 30 per cent of the γ,δ-unsaturated acid was obtained. Both of the dihydro acids are stable under the conditions used. The preponderance of form III over form IV may possibly be due to the tendency of the double bond to

become conjugated with the phenyl group. In the case of vinylacrylic acid, where R = II and there are no other directing substituents, reduction by sodium amalgam in sodium carbonate solution leads to terminal addition of hydrogen (formula III) (54, 297), but in acetic acid solution there is a substantial amount (18 per cent) of the γ,δ-unsaturated acid formed (54).

Sorbic acid, $CH_3CH{=}CH-CH{=}CH-COOH$, has been shown by many workers (54, 86, 116) to give nearly a 50–50 mixture of the β,γ- and γ,δ-hexenoic acids when reduced with sodium or aluminum amalgams; the pH of the solution causes a slight variation in the relative amounts. The methylsorbic acids likewise give both forms III and IV (54), although in earlier work (18, 257) the reduction was reported to occur terminally only. With vinylogs of sorbic acid, however, Kuhn and Hoffer obtained only terminal reduction with sodium amalgam (174).

In the diene acids where the carboxyl group is in the middle of the chain, a crossed conjugated system is present. It might be expected that the doubly conjugated ethylene group would be the one attacked, and from the limited number of cases studied, this would seem to be true. α-Vinylcinnamic acid (V) is reduced by sodium amalgam, in neutral solution, to α-vinylhydrocinnamic acid (VI), which rearranges to the conjugated isomer (VII) in the presence of base (136). Kuhn (173) originally considered that VII was the primary reaction product.

$$C_6H_5CH{=}CCOOH \quad \xrightarrow[\text{NaHCO}_3]{\text{Na amalgam}} \quad C_6H_5CH_2CHCOOH \quad \xrightarrow{\text{NaOH}}$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad CH{=}CH_2 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad CH{=}CH_2$$

V   VI

α-Vinylcinnamic acid α-Vinylhydrocinnamic acid

$$C_6H_5CH_2CCOOH$$
$$\quad\quad\quad\quad ||$$
$$\quad\quad CH-CH_3$$

VII
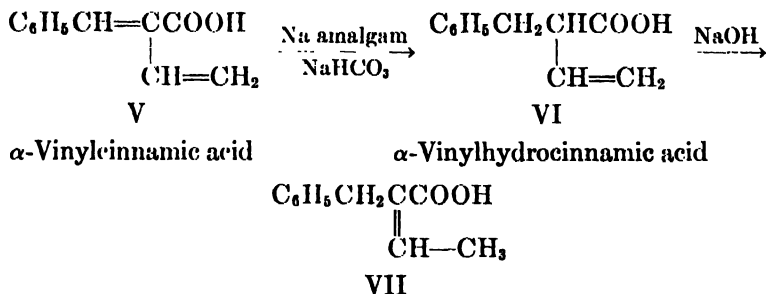
α-Styrylcinnamic acid (VIII) is also reduced at the α,β-double bond by sodium amalgam (136, 290); the product (IX) in this case is stable, since the remaining double bond is conjugated to a phenyl group.

$$C_6H_5CH{=}CCOOH \quad \xrightarrow{\text{Na amalgam}} \quad C_6H_5CH_2CHCOOH$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad CH{=}CHC_6H_5 \quad\quad\quad\quad\quad\quad\quad CH{=}CHC_6H_5$$

VIII   IX

α-Styrylcinnamic acid
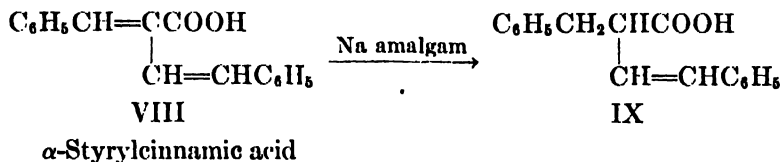
With the 2,3-dicarboxylic acid derivatives of butadiene, reduction by sodium amalgam leads to the saturated acids (290). Thus, 1,4-diphenylbutadiene-2,3-dicarboxylic acid yields a mixture of the meso and dl forms of the butane diacids, in which the former predominates.

Very little work has been reported on the reduction of diene ketones and aldehydes. Evans and Farmer (86) found that crotylideneacetone, $CH_3CH=CH-CH=CHCOCH_3$, is reduced to a dimolecular compound by aluminum amalgam. Fischer and Wiedmann (107) obtained reduction of the ethylene double bond adjacent to the carbonyl group in crotylideneacetone and cinnamalacetone by fermenting yeasts. The reduction of sorbic aldehyde and its vinylog, $CH_3CH=CH-CH=CH-CH=CH-CHO$, by yeasts led to saturation of the α,β-double bond, and conversion of the aldehyde group to a primary alcohol.

Table 12 contains a summary of the work reported in this field.

III. ELECTROLYTIC REDUCTION

A. Introduction

In the electrolytic reduction of organic compounds there are many variables to be considered; therefore the results are not as susceptible to generalization as are those of chemical reduction and catalytic hydrogenation. The hydrogen overvoltage of the cathode material, the cathodic potential and current density, the hydrogen-ion concentration of the medium, the purity and history of the cathode material, and the presence or absence of various inhibitors and promoters all affect the results. These subjects have been thoroughly discussed in recent reviews (114, 294) and books (51, 113), and are beyond the scope of this article.

The cathodes used may be divided into two large classes: (1) *Those of low overvoltage:* In this class belong cathodes of iron, nickel, platinum, and palladium. These cathodes are rarely effective if used smooth; it is generally necessary to coat them with a deposit of the finely divided metal (242) or to add to the solution a nickel or palladium salt (108). When so treated they bring about the reduction of many substances, and the course of the reaction resembles that taken by catalytic hydrogenation (332). (2) *Those of high overvoltage:* In this class belong cathodes of copper, lead, mercury, zinc, tin, and cadmium. These cathodes may be used in the form of the smooth metal, or the surface may be roughened by alternate reduction and oxidation, or it may be amalgamated with mercury. The presence of small traces of more noble metals in these cathodes lowers the overvoltage considerably, and thereby destroys or diminishes the effectiveness of the cathode (182, 210, 295). Reductions brought about by the cathodes of this class resemble reductions by chemical agents, especially sodium amalgam (182, 210, 332). Sometimes the electrodes of class 1 can be made to resemble those of class 2 by adding to the electrolyte a small amount of certain metal salts, especially those of titanium, chromium, vanadium, iron, and cerium (113), in which case probably the reduced form of the salt is the true reducing agent.

There have been several theories proposed to account for reduction at the cathodes of class 2 (see 332); it has been suggested that nascent hydrogen atoms constitute the active reducing agent, or that hydrogen gas, liberated below the normal potential for hydrogen evolution, reacts with the unsaturated compound.

TABLE 12
Reduction of diene acids, aldehydes, and ketones by chemical reducing agents

COMPOUND REDUCED	REDUCING AGENTS AND CONDITIONS	DIHYDRO COMPOUNDS FORMED	REFERENCES
Vinylacrylic acid .... $\overset{4}{CH_2}=\overset{3}{CH}\overset{2}{CH}=\overset{1}{CH}COOH$	Na amalgam, NaHCO₃ solution	100% 1,4-	(116, 54, 297)
Sorbic acid........ $\overset{4}{CH_3}\overset{3}{CH}=\overset{2}{CH}\overset{1}{CH}=CHCOOH$	Na amalgam, NaHCO₃ solution	80% 1,4-	(145)
	Na amalgam, acetic acid	82% 1,4-; 18% 1,2-	(54)
	Na amalgam, neutral or acid solution	Mixture of 1,2- and 1,4-	(116, 86)
	Na amalgam, neutral	40% 1,2-; 60% 1,4-	(175)
	Na amalgam, NaHCO₃ solution	40% 1,2-; 60% 1,4-	(54, 332)
	Na amalgam, acetic acid	55% 1,2-; 45% 1,4-	(54, 332)
	Al amalgam, neutral or alkaline solution	30-40% 1,2-; 70-60% 1,4-	(116)
	Al amalgam, neutral or alkaline solution	45% 1,2-; 55% 1,4-	(143)
	Devarda's alloy, NaOH	41% 1,2-; 59% 1,4-	(332)
α-Methylsorbic acid............ $\overset{4}{CH_3}\overset{3}{CH}=\overset{2}{CH}CH=\overset{1}{C}COOH$ $\mid$ CH₃	Na amalgam, weakly acid	1,4-Reduction	(18, 19)
α-Ethylsorbic acid........... $\overset{4}{CH_3}\overset{3}{CH}=\overset{2}{CH}CH=\overset{1}{C}COOH$ $\mid$ C₂H₅	Na amalgam, weakly acid	1,4-Reduction	(18, 19)
β-Methylsorbic acid......... $\overset{4}{CH_3}\overset{3}{CH}=\overset{2}{CH}C=\overset{1}{CH}COOH$ $\mid$ CH₃	Na amalgam, NaHCO₃ solution	28% 1,2-; 72% 1,4-	(54)
	Na amalgam, weakly acid	1,4-	(19)

γ-Methylsorbic acid.......... $CH_3CH=CCH=CHCOOH$ (with CH_3 substituent)	Na amalgam, weakly acid	1,4-	(18, 19)
β,δ-Dimethylsorbic acid....... $CH_3C=CHC=CHCOOH$ (with CH_3, CH_3 substituents)	Na amalgam, acid or alkaline	1,4-	(18, 19)
	Na amalgam, $NaHCO_3$ solution	1,4-	(257, 258)
Crotylidenemalonic ester....... $CH_3CH=CHCH=C(COOC_2H_5)_2$	Na amalgam, $NaHCO_3$ solution	38% 1,2-; 62% 1,4-	(54)
	Al amalgam, neutral	Dimolecular	(62)
Cyanosorbic ester .... $CH_3CH=CHCH=CCOOC_2H_5$ (with CN substituent)	Al amalgam, neutral	Dimolecular	(62)
Octatrienoic acid............ $CH_3CH=CHCH=CHCH=CHCOOH$	Na amalgam, $NaHCO_3$ solution	1,6-	(174)
Decatetraenoic acid.......... $CH_3(CH=CH)_4COOH$	Na amalgam, $NaHCO_3$ solution	1,8-	(174)
Cinnamylideneacetic acid...... $C_6H_5CH=CHCH=CHCOOH$	Na amalgam, neutral solution	1,4-	(257)
	Na amalgam, $NaHCO_3$ solution $TiCl_3$, NH_4OH	1,4-	(18, 19) (150)
α-Vinylcinnamic acid.........	Na amalgam, $NaHCO_3$ or acetic acid solution	1,2- chiefly 1,2- chiefly	(136)
α-Styrylcinnamic acid... $C_2H_5CH=CCH=CH_2$ (with COOH substituent)	Na amalgam, $NaHCO_3$ solution	1,4- (rearrangement)	(173)
	Al amalgam, neutral Na amalgam, Na_2CO_3 solution	1,2- chiefly 1,2-	(136) (136)
$C_6H_5CH=CCH=CHC_6H_5$ (with COOH substituent)	Na amalgam, acetic acid	1,2-	(136, 290)

TABLE 12—Concluded

COMPOUND REDUCED	REDUCING AGENTS AND CONDITIONS	DIHYDRO COMPOUNDS FORMED	REFERENCES
β-Phenylsorbic acid 4 3 2 1 $CH_3CH=CHC=CHCOOH$ ‖ C_6H_5	Na amalgam, neutral solution	30% 1,2-; 70% 1,4-	(175)
α-Phenylcinnamylideneacetic acid 4 3 2 1 $C_6H_5CH=CHCH=CCOOH$ ‖ C_6H_5	Na amalgam, neutral solution	1,4-	(257)
Muconic acid 1 2 3 4 $HOOCCH=CHCH=CHCOOH$	Na amalgam	1,4- entirely. The *trans-trans* gives the *trans* 1,4-; the *cis-cis* gives the *cis* 1,4-dihydro acid	(93)
	Al amalgam, neutral, acid, or basic solution	1,4- entirely	(86)
Ethyl muconate	Na amalgam, weakly basic	1,4- entirely	(93)
2,3-Diphenylmuconic acid 1 2 3 4 $HOOCCH=C—C=CHCOOH$ ‖ ‖ C_6H_5, C_6H_5	Na amalgam, NaHCO₃ solution	No dihydro; mixture of meso (chiefly) and some *dl* saturated acid	(290)
2,3-Dicarboxy-1,4-diphenylbutadiene 1 2 3 4 $C_6H_5CH=C—C=CHC_6H_5$ ‖ ‖ HOOC COOH	Na amalgam, NaHCO₃ solution	No dihydro; 80% *dl*, 20% meso saturated	(290)
2,3-Dicarboxy-1,1,4-triphenylbutadiene 1 2 3 4 $(C_6H_5)_2C=C—C=CHC_6H_5$ ‖ ‖ HOOC COOH	Al amalgam, neutral solution	80% dimolecular	(86)
Crotylideneacetone 4 3 2 1 $CH_3CH=CHCH=CHCOCH_3$	Yeast, neutral	1,2-Dihydro	(107)

Sorbic aldehyde.......... $\overset{4}{C}H_3\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}H=CHCHO$	Na or Al amalgam	Non-distillable	(107)
	Yeast, neutral solution	4-Hexen-1-ol	(107)
	Fe, acetic acid	Saturated aldehyde and alcohol	(358)
	Na amalgam, faintly acid, cold	1,4-Dihydro and polymers	(107)
Cinnamylideneacetone...... $\overset{4}{C_6H_5}\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}H=CHCOCH_3$	Yeast, neutral solution	1,2-	(107)
	Al amalgam	Terminal dihydro	(149, 150)
α-Crocetin.........	TiCl₃, NH₄OH or NaOH	Terminal dihydro; if use large excess of reagent may get hexahydro compound	(149)

Because of the close resemblance between the electrolytic reduction of sorbic acid by the cathodes of this class, and the chemical reduction of sorbic acid by sodium and aluminum amalgams, Wilson (332) has suggested that the two processes have the same mechanism, and has postulated that the mechanism used by Burton and Ingold (54) to explain reduction by dissolving metals can also be applied to electrolytic reduction at high-overvoltage cathodes (see section II B).

Electrolytic reduction at the cathodes of class 1 is probably a catalytic reaction; the hydrogen liberated at the cathode surface adds to the unsaturated compound under the catalytic influence of the finely divided metal surface (332).

B. Reduction of unsaturated hydrocarbons

Practically no work has been reported on the electrolytic reduction of ethylenic hydrocarbons, but several unsaturated acids have been studied in which the double bond is sufficiently far removed from the carboxyl group so that there is little influence of one group on the other. In view of the analogies presented above, such acids should not be reduced at the high-overvoltage cathodes, but should be saturated at cathodes of spongy nickel or platinum. These predictions are realized: linoleic, undecylenic, allylacetic, and allylmalonic acids are reduced to the saturated acids at a nickel cathode covered with spongy nickel (242), and oleic acid has been reduced to stearic acid at a spongy-nickel cathode (242) and at a platinized cathode (210), but it is not attacked when cathodes of lead, mercury, or copper are used (198, 332).

Acetylenes are reduced electrolytically at the cathodes of class 1, and the course of the reaction is very similar to that of catalytic hydrogenation. Acetylene itself is reduced at a platinized-platinum cathode, in acid or basic medium, to a mixture of ethylene and ethane. By adjusting the current density the reaction can be controlled to give ethylene alone; at higher current densities the reduction is more vigorous, and ethane is formed (36). Dialkylacetylenes are reduced at a spongy-nickel cathode, to the *cis* olefins (61); these are also the products formed when the dialkylacetylenes are hydrogenated catalytically in the presence of Raney nickel (56). It might be expected that the dialkylacetylenes, which can be reduced by sodium in liquid ammonia (but not by sodium and alcohol) (56), would be reduced electrolytically at the cathodes of class 2, but even with amalgamated lead the potential is not sufficiently high, and no reduction occurs (61). Dimethylethinylcarbinol is reduced to the olefinic carbinol, however, in high yields at a copper cathode, and this process is said to have been used in Russia on a semi-commercial scale (100, 101); similarly, methylcyclopropylethinylcarbinol is reduced at a copper cathode to give a 60 to 70 per cent yield of the olefin (118, 119). Monovinylacetylene is reduced to butadiene in good yields at a platinum black electrode (192).

The polynuclear hydrocarbons, which can be reduced both catalytically and by dissolving metals, should be capable of reduction at cathodes of either class. From the limited data available, this would seem to be the case. Anthracene is converted to 9,10-dihydroanthracene at a mercury cathode in alkaline solution,

just as it is by sodium and aluminum amalgams (332).   Phenanthrene is reduced in acid solution at a spongy-palladium cathode to the same tetrahydro derivative that is obtained by catalytic hydrogenation over palladium black (49).

C. Reduction of unsaturated acids, aldehydes, and ketones

α,β-Unsaturated acids are comparatively easily reduced to the saturated acids by electrodes of either class; usually a platinized-platinum or a spongy-nickel cathode is used in acid solution (108, 242), and a mercury cathode in alkaline solution (242); with cinnamic acid a tin or lead cathode is also effective (217, 218).   Ordinarily the saturated acid is the only product, but occasionally the carboxylic acid group is attacked.   Thus, cinnamic acid at a lead dioxide cathode forms hydrocinnamyl alcohol and a dimeric product, indicating the intermediate formation of an aldehyde (138).

$$C_6H_5CH{=}CHCOOH \longrightarrow C_6H_5CH_2CH_2COOH \longrightarrow$$

Cinnamic acid

$$C_6H_5CH_2CH_2CHO \nearrow \begin{array}{l} C_6H_5CH_2CH_2CHOH \\ \quad\quad\quad\quad | \\ C_6H_5CH_2CH_2CHOH \end{array}$$
$$\searrow C_6H_5CH_2CH_2CH_2OH$$
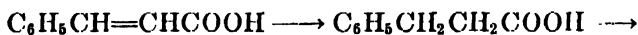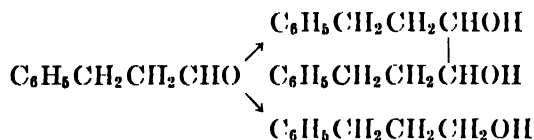
The reduction of benzoic acid at a mercury or lead cathode is of considerable interest, and shows a close resemblance to the reduction of this acid by sodium amalgam.   In alkaline solution, at these cathodes, nuclear reduction occurs, and tetrahydrobenzoic acid is obtained; sodium amalgam in alkaline solution produces the same result (210).   If the electrolytic reduction is carried out in acid solution, the carboxyl group is attacked, and benzyl alcohol is obtained in high yield (69); sodium amalgam in acid solution is reported to give benzyl alcohol also (see 210).

Tetrahydrobenzoic acid   Benzoic acid   Benzyl alcohol
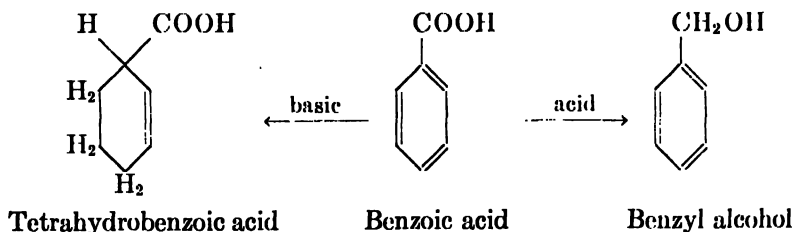
With unsaturated aldehydes and ketones, electrolytic reduction is usually accomplished at a lead or copper cathode.   In acid solution, at a lead cathode, organometallic compounds may be formed; this does not occur in neutral or alkaline solution (182), or with electrodes of copper, tin, zinc, or amalgamated lead.   Reduction at these cathodes resembles reduction by sodium and by sodium amalgam.   Thus, the reaction does not always stop at the saturated carbonyl compound, but may proceed further, to give the saturated alcohol, or dimerization may occur.

Crotonaldehyde and cinnamaldehyde are reduced at a lead cathode to the saturated alcohol (182), but with mesityl oxide a variety of compounds is formed, including desoxymesityl oxide, which probably arises from a dimeric, pinacol-type reduction:

$$(CH_3)_2C=CHCOCH_3 \rightarrow \begin{array}{c} CH_3COCH_2C(CH_3)_2 \\ | \\ CH_3COCH_2C(CH_3)_2 \end{array} \rightarrow (CH_3)_2C \begin{array}{c} CH_2-CCH_3 \\ | \\ C-CCOCH_3 \end{array}$$

Mesityl oxide
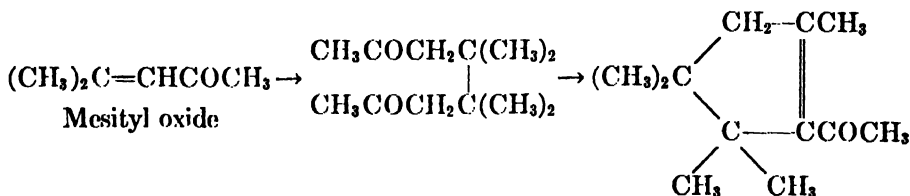
Diene acids

The striking analogies between electrolytic reduction on the one hand, and reduction by dissolving metals or by catalytic methods on the other, have been brought out by Wilson (332) and Isaacs and Wilson (143, 144, 145) from a study of the reduction of the butadiene acids, especially sorbic acid. This acid is reduced by sodium amalgam, aluminum amalgam, or Devarda's alloy, to a mixture of the 1,2- and 1,4-dihydrosorbic acids (I and II); it is not reduced by magnesium or iron. Electrolytically, it is attacked at a mercury, cadmium, copper, or tin cathode, and the products are again mixtures of the 1,2- and 1,4-dihydro acids. As table 13 shows, the analogy is close, and the composition of the product is independent of the reducing agent; this argues for a common mechanism for the electrolytic and chemical reduction processes.

Catalytically, with the Adams catalyst, sorbic acid absorbs 1 mole of hydrogen to give a mixture of the completely saturated acid, unreduced sorbic acid, and some of the 3,4-dihydro compound (III); a similar mixture is obtained when sorbic acid is reduced at cathodes of class 1, that is, at a platinized-platinum cathode. The parallel is not so close between reduction at a spongy-nickel cathode and catalytic hydrogenation with Raney nickel (see table 14).

$$CH_3CH=CHCH_2CH_2COOH \qquad CH_3CH_2CH=CHCH_2COOH$$

I   II

1,2-Dihydrosorbic acid   1,4-Dihydrosorbic acid

$$CH_3CH_2CH_2CH=CHCOOH$$
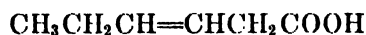
III

3,4-Dihydrosorbic acid

Vinylacrylic acid on reduction with sodium amalgam yields the 1,4-dihydro compound as the principal product; this also predominates when the acid is reduced electrolytically at a copper or mercury cathode in alkaline solution (145). When reduced catalytically, vinylacrylic acid gives a mixture of the 3,4-dihydro and the tetrahydro acids (221); at a spongy-nickel electrode Isaacs and Wilson

report it to give the 3,4-dihydro and tetrahydro acids (145), although Muskat and Knapp (222) had considered the main product to be the 1,2-dihydro derivative.

IV. CATALYTIC HYDROGENATION

A. Introduction

Hydrogen can be added in the presence of a catalyst to practically any carbon–carbon multiple bond. Since the ease of addition varies widely with the position of the unsaturation and with the nature of the adjacent groups, selective hydro-

TABLE 13

Reduction of sorbic acid at high-overvoltage cathodes (332)

REDUCING AGENT	PER CENT OF 1,2-REDUCTION IN		
	NaOH	NaHCO₃	CH₃COOH
Mercury cathode................................	40	41	54
Cadmium cathode.............................	39	40	54
Copper cathode.............................	40		50
Sodium amalgam................................		40	55
Aluminum amalgam.............................	45	45	
Devarda's alloy.............................	41		

TABLE 14

Reduction of sorbic acid at low-overvoltage cathodes (332)

REDUCING AGENT	MEDIUM	PER CENT 3,4-DIHYDRO	PER CENT 1,2- + 1,4-DIHYDRO	PER CENT SATURATED ACID
Spongy-nickel cathode.................	70% acetic acid	19	18	63
Platinized-platinum cathode...........	70% acetic acid	46	5	49
H₂ + Raney nickel....................	Alcohol	86	10	3
H₂ + Adams catalyst.................	Alcohol	38	7	55

genation of one unsaturated group and not another can frequently be attained by a suitable choice of catalyst and conditions.

A great number of hydrogenation catalysts have been developed, and it is beyond the scope of this article to discuss them in detail. For a comprehensive review of hydrogenation catalysts and their preparation, the reader is referred to the texts of Ellis (84) and of Berkman, Morrell, and Egloff (34). The ease of hydrogenation, and sometimes the course of this reaction, may vary, not only with different catalytic metals, but also with different methods of preparing a given metal catalyst; consequently for laboratory use those catalysts are most satisfactory the preparation of which is simplest and gives on repetition material of uniform and reproducible activity. For this reason the Adams platinum and palladium oxide–black catalysts (162), the Raney nickel catalyst (67, 219a),

and certain forms of reduced nickel and copper chromite catalysts (4) are of more value, in general, than are the platinum black catalyst of Willstätter (331), the various forms of colloidal platinum and palladium (41, 232, 284, 287), and many of the mixed nickel oxide catalysts.

Because the activity of many catalysts is greatly affected by small traces of impurities, acting as promoters or poisons, and varies from batch to batch, there are many discrepancies between the results of different workers, and a certain amount of caution must be exercised in evaluating literature data. Furthermore, many catalysts age on standing (95, 321) or show varying amounts of fatigue in a reaction (309), so that they no longer give the same results as when fresh, and this has also been a fruitful source of contradictions.

Solvents play an important rôle in determining the ease with which a given substance undergoes hydrogenation (4, 142, 271), and, of course, so do temperature and pressure. The effect of these various experimental conditions, the commercial applications of catalytic hydrogenation, and the various theories have been adequately discussed in recent reviews and texts (4, 34, 84, 270, 326, 274a) and will not be considered here in detail.

B. Hydrogenation of olefins

In the case of olefins, hydrogenation can be brought about by a wide variety of catalysts and under many experimental conditions. Palladium and platinum catalysts, either as finely divided metals or in the colloidal state, and Raney nickel, will bring about the saturation of most olefins at room temperature and at pressures varying from below atmospheric to 2–3 atm. Reduced nickel catalysts can be used at higher temperatures, either in the Sabatier–Senderens technique or under elevated pressures. Copper and cobalt catalysts have been used, although they are less active than nickel and require higher temperatures and pressures. Copper chromite will catalyze the reduction of olefins but is, in general, less effective than nickel or other catalysts (4). Amorphous chromium oxide is also effective, but not the oxides of zinc, manganese, or magnesium (308). Since in the reduction of olefins, high temperatures and pressures may bring about cracking, polymerization, or other side reactions, if it is desired simply to hydrogenate the substance, the platinum, palladium, and active nickel catalysts, which are effective at pressures of 2 to 3 atm., are the ones of choice. Occasionally even these pressures are too high,– as with olefinic carbinols, which may undergo cleavage,– and then the reaction can be carried out at reduced pressures (85, 125).

In contrast to chemical methods, simple olefins are usually hydrogenated catalytically more easily than are conjugated olefins or α,β-unsaturated carbonyl compounds (162), and aryl double bonds are the most difficult to hydrogenate. The reduction of carvone furnishes a good example of the effect of conjugation. In the presence of platinum black or reduced nickel the isolated double bond is saturated first, whereas with zinc and acetic acid, or sodium and alcohol, the conjugated double bond is reduced first (15).

CH₃
|
O   H₂   C=CH₂
‖ |
H   —H   Na
| |H₂   ⟵   alcohol
H₃C   H₂

O   H₂   H   CH₃
‖ | |
—C=CH₂   catalytic
| |H₂   hydrogenation   ⟶
H₃C   H

Carvone

O   H₂   H   CH₃
‖ | /
—CH
| |H₂   \
H₃C   H   CH₃
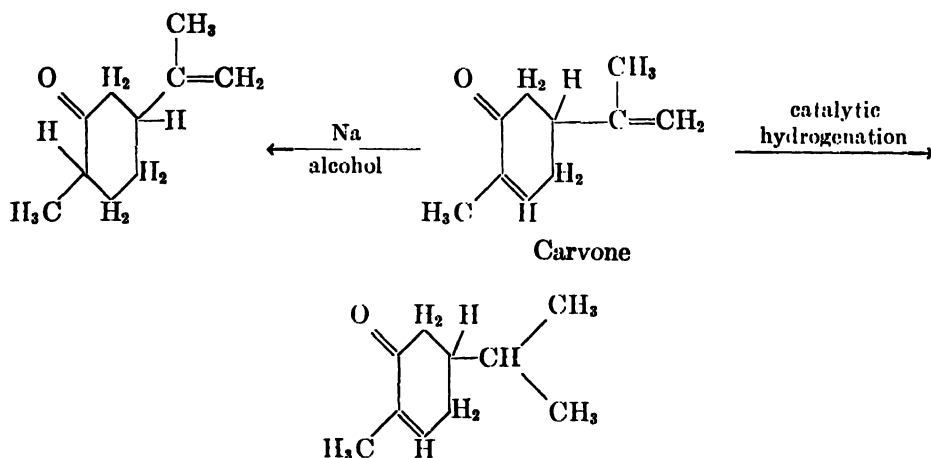
Farmer and Galley (96) observed that the rate of hydrogenation of unsaturated acids increased as the double bond was removed from the carboxyl group (see 129 also). This generalization as to the effect of conjugation does not always hold, however, for in the hydrogenation of citral the conjugated ethylene bond is the first one attacked.

Numerous studies have been made in an effort to determine the effect of structure on the ease of hydrogenation of olefins. Except in a qualitative way, these attempts have not been highly successful, for many other factors contribute to the results, including the weight of the catalyst (309), the solvent (271), the degree of purity of all reagents used, the rate of diffusion of the hydrogen to the catalyst (309), and others. Kailan and Hartel (148) have shown that reproducible rates of hydrogenation cannot be obtained unless all of the conditions are exactly reproduced and samples of catalyst from the same batch are used. In general, a comparison between two compounds, especially if they are very similar in structure, is not reliable unless the hydrogenations are carried out under identical conditions, using the same concentrations, solvents, weights and batch of catalyst, etc. Farkas (91) emphasized this point in saying, "Observed rates of hydrogenation are not comparable unless it is ascertained that the concentrations of the hydrogen and unsaturated compound in the adsorption layer are comparable in the different experiments."

In spite of these difficulties, certain generalizations can be made. Lebedev and his coworkers (186) found that when platinum black is used as the catalyst, monosubstituted olefins, $RCH=CH_2$, are reduced very rapidly, and the rate is constant or nearly so throughout the reaction. Olefins of the type $RCH=CHR'$ are reduced more slowly, and the rate declines toward the end. Unsymmetrically disubstituted olefins, $R_2C=CH_2$, show a gradual decline in rate. Tri- and tetra-substituted olefins, $R_2C=CHR'$ and $R_2C=CR_2$, are reduced still more slowly, and aryl and carboxyl groups also slow down the rate. Kern, Shriner, and Adams (162) obtained similar results, which are recorded in table 15. Zartman and Adkins (357) also found that arylolefins are hydrogenated more

slowly than aliphatic when nickel–kieselguhr and copper chromite catalysts are used.

Kazanskii and Tatevoysan (159) confirmed the work of Adams as to the deactivating effect of aryl groups when platinum is the catalyst, and reported the following sequence:

$$CH_3CH=C(C_2H_5)_2 > CH_3C=CHCH_3 > CH_3CH=C(C_6H_5)_2 >$$
$$\overset{|}{C_6H_5}$$

$$(C_6H_5)_2C=CHC_6H_5$$
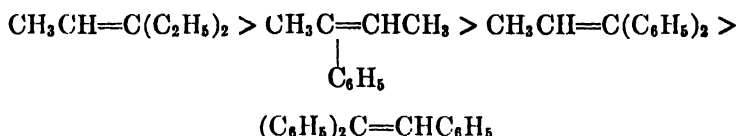
When, however, palladium black is used, aryl groups increase the ease of hydrogenation, and these workers obtained a sequence the exact reverse of the one given above (160). A similar reversal with platinum and palladium has been observed by Yurashevskii (342, 343), who found that with palladium as catalyst, four aryl groups were necessary before a retarding influence was noticed.

TABLE 15

Hydrogenation of olefins with platinum black (162)

OLEFIN	TIME FOR HYDROGENATION
	minutes
Eugenol	3.5
Undecylenic acid	2.5
Styrene	9
1,1-Diphenylethylene	21
Stilbene	69

Dupont (73) has found that Raney nickel catalyst gives results similar to platinum black as concerns the effect of substitution around the double bond. He obtained the following sequence:

$$RCH=CH_2 > RCH=CHR' > R_2C=CH_2 \quad and \quad R_2C=CHR'$$
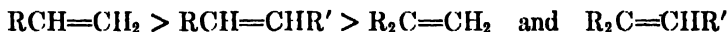
The size and degree of branching of the alkyl groups also has an effect on the rate of hydrogenation. Lagerev (179, 180), in a study of the hydrogenation of isomeric hexenes over platinum black, obtained the following sequences for rates of hydrogenation:

$$(n)\text{-}C_3H_7CH=CHCH_3 > (CH_3)_2CHCH=CHCH_3 > (CH_3)_2C=C(CH_3)_2$$
$$(n)\text{-}C_4H_9CH=CH_2 > (CH_3)_3CCH=CH_2 > C_2H_5C=CHCH_3 > C_2H_5CH=C(CH_3)_2$$
$$\overset{|}{CH_3}$$
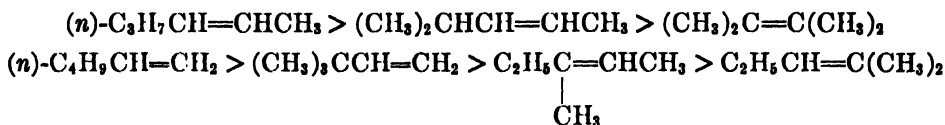
Schuster (275) found that the size of the alkyl group is of great importance; using nickel on activated charcoal as catalyst, he obtained the half-time periods shown in table 16. Schmidt (271), on the other hand, found no particular influence due to the size of the R group in monosubstituted olefins.

In an effort to avoid the difficulties due to poisons, catalyst fatigue, solvents,

and other variables, many workers have attempted to determine the relative ease of hydrogenation of two olefins by studying the distribution of hydrogen between them when a mixture of the two is treated with an insufficient quantity of hydrogen. By using one olefin as a reference compound, a series of relative reactivities can be set up. Vavon (310) and Vavon and Jakes (315, 316), who were among the first to use this technique, used α-pinene as reference, since the amount of it remaining unreduced could be easily determined by a measurement of the optical rotation. In this way the data in table 17 were obtained. These

TABLE 16

Effect of size of alkyl group on rate of hydrogenation

COMPOUND	HALF-TIME
	minutes
Ethylene	8
Propylene	104
1-Butene	225
2-Methylpropene ("isobutene")	1100

TABLE 17

Hydrogenation of olefins in admixture with α-pinene (310, 316)

COMPOUND	PER CENT HYDROGENATED
$(n)C_3H_7CH{=}CHC_2H_5$	96
$C_2H_5CH{=}C(CH_3)_2$	71
$CH_3CH{=}C(C_2H_5)_2$	70
$(CH_3)_2C{=}CC_2H_5$ $\quad\mid$ $\quad CH_3$	65
$C_6H_5CH{=}CHCOOH$	65
$C_6H_5C{=}CHCOOH$ $\quad\mid$ $\quad CH_3$	32
$C_6H_5CH{=}CCOOH$ $\qquad\mid$ $\qquad CH_3$	22
$C_6H_5C{=}CCOOH$ $\quad\mid\quad\mid$ $H_3C\ \ CH_3$	18

results are in general agreement with those mentioned above with regard to the effect of degree of substitution of the double bond.

In a modification of this type of study, Lebedev (186, 187) found that a mixture of olefins of the same degree of substitution is hydrogenated concurrently, with no break in the curve, whereas if the two olefins are of different degrees of substitution they are hydrogenated consecutively, and there is a break in the curve. By using olefins of known structures as reference substances, it is possible in this way to determine the degree of substitution of an unknown olefin.

Similar results have also been obtained by Farmer and Galley (95, 96).   Davis, Thompson, and Crandall (68) have also confirmed Lebedev's work, and have determined by fractionation and analysis the composition of the mixture obtained by adding about 50 per cent of the theoretical amount of hydrogen to the mixture of two olefins. A summary of their data is given in table 18.

Conclusions regarding relative ease of hydrogenation drawn from competitive hydrogenations are not, however, always valid, as Adkins and his students (7) have shown.   They found that the results obtained when two substances were hydrogenated individually and in a mixture were not always concordant.   For example, a given amount of pinene alone was hydrogenated in 5 min., whereas allyl alcohol required 34 min.; but when one molar equivalent of hydrogen was added to an equimolar mixture of pinene and allyl alcohol, 92 per cent of the alcohol was reduced, and only 8 per cent of the pinene.

The effect of geometrical configuration of the double bond on ease of hydrogenation has received some attention.   In a series of carefully conducted experiments, Paal and Schiedewitz (233, 234, 235) have found that cis α,β-un-

TABLE 18

Hydrogenation of mixtures of olefins over platinum catalyst (68)

COMPONENTS OF MIXTURE		PER CENT OF EACH HYDROGENATED (USING INSUFFICIENCY OF HYDROGEN)	
I	II	Per cent of I	Per cent of II
Propene	2-Butene	90	20
1-Butene	2-Butene	79	21
"Isobutene"	Trimethylethylene	96	44
Isopropylethylene	Trimethylethylene	93	20

saturated acids are reduced more rapidly than their *trans* isomers, when colloidal palladium–barium sulfate is the catalyst.   Similarly, *cis*-stilbene is hydrogenated more rapidly than *trans*-stilbene (234).   The greater ease of hydrogenation of the *cis* forms may be due to the fact that the *cis* olefins are more strongly adsorbed on the catalyst than the *trans* (241).   The *cis* form is not, however, always hydrogenated more rapidly than its *trans* isomer.   Weygand, Werner, and Lanzendorf (322) found that while the *cis* forms of p,p'-dimethyl- and p,p'-dibutyl-dibenzoylethylenes were hydrogenated more rapidly than the *trans* forms, with the monosubstituted p-methyl- and p-butyl-dibenzoylethylenes, the *trans* form was hydrogenated the more rapidly.
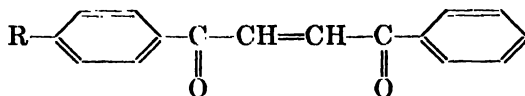
Schuster (275), using a nickel–charcoal catalyst, could observe no difference in the half-time period required for the reduction of the *cis* and *trans* forms of 2-butene.   Wessely and Wellaba (320a) found but little difference in the velocity

of hydrogenation of the *cis* and *trans* forms of dimethylstilbene, using palladium sponge as catalyst. Campbell and Kerwin (58) have found that the relative velocity of hydrogenation of the *cis*- and *trans*-4-octenes can be reversed by a change of solvent or catalyst; in ethyl alcohol with Raney nickel the *cis* form was hydrogenated much more rapidly, but when platinum oxide–platinum black was used, the *trans* form was the more rapidly reduced.

In the hydrogenation of olefins under moderate conditions, few side reactions occur. In the case of the higher unsaturated acids some migration of the double bond does take place, however. Hilditch and Vigarthi (129) showed that when $\Delta^{9,10}$-octadecenoic ester is reduced at 115°C. with a nickel catalyst, and an insufficiency of hydrogen is used, the unsaturated part of the product contains the *cis* and *trans* forms of the $\Delta^{8,9}$-, $\Delta^{9,10}$-, $\Delta^{10,11}$-ethylenic acids.

Olefinic double bonds can sometimes be hydrogenated without the use of hydrogen gas. Cinnamic acid is reduced to hydrocinnamic acid by treatment with platinum black in boiling tetralin, the solvent being oxidized to naphthalene (164).

C. Selective hydrogenation

When there are two or more unsaturated groups in a molecule, the question arises as to which of these will be hydrogenated first. The answer, of course, depends on the nature of the two groups, the catalyst used, and the experimental conditions.

The aliphatic ethylene group is so easily hydrogenated that when it is present in a molecule together with an aryl nucleus or a carboxyl or carbalkoxyl group the ethylene bond is almost always hydrogenated first. This is true for arylolefins and for olefinic acids and esters with platinum, palladium, Raney nickel, many nickel and nickel oxide catalysts, copper chromite, etc. There are some exceptions. If the aryl nucleus is activated, or if the experimental conditions are strenuous, it may be saturated more or less simultaneously with the ethylene group. Thus Ipatieff (139, page 250) has shown that olefinic phenols are reduced to alkylphenols in the presence of copper oxide at 290°C., but with a nickel catalyst simultaneous saturation of the side chain and of the nucleus occurs. With copper oxide allylbenzene is reduced only in the side chain, but if nickel oxides are used, cyclohexylpropane is obtained (34). Sauer and Adkins (263) have shown that butyl oleate in the presence of zinc chromite at 300°C. undergoes selective saturation of the carboxyl group, yielding octadecenol, but if copper chromite is used, the product is the saturated alcohol. Komari (171a) reported that the ethyl esters of ricinoleic and erucic acids can be reduced to the unsaturated alcohols by an iron–chromium oxide catalyst at 320°C.

With unsaturated aldehydes and ketones, selective hydrogenation of the ethylenic group is more difficult; in many cases, especially with aldehydes, it is not possible, and the product obtained is the saturated alcohol, or even the saturated hydrocarbon (70, 292). In other cases the saturated carbonyl compound is the first product formed, and in still others, the carbonyl group may be attacked first (70). Adams and his coworkers (2, 48, 152, 306) found that the

platinum oxide- platinum black catalyst, in the presence of small amounts of ferrous ion and zinc acetate, causes preferential hydrogenation of the carbonyl group in many α-β-unsaturated aldehydes, leading to unsaturated alcohols in good yields. This is true for cinnamaldehyde, furfural, citral, and others. For citral the course of hydrogenation has been shown to be as follows:

$$(CH_3)_2C=CHCH_2CH_2C=CHCHO$$
$$|$$
$$CH_3$$

Citral

$$\downarrow$$

$$(CH_3)_2C=CHCH_2CH_2C=CHCH_2OH$$
$$|$$
$$CH_3$$

Geraniol

$$\downarrow$$

$$(CH_3)_2C=CHCH_2CH_2CHCH_2CH_2OH$$
$$|$$
$$CH_3$$

Citronellol

$$\downarrow$$

$$(CH_3)_2CHCH_2CH_2CH_2CHCH_2CH_2OH$$
$$|$$
$$CH_3$$
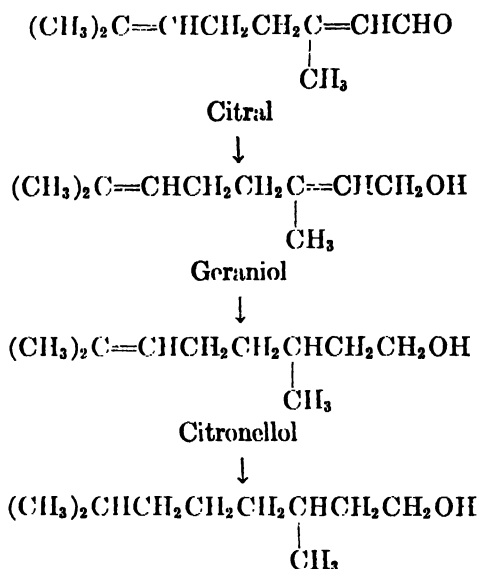
Thompson has found that this effect of ferrous sulfate is nullified if the reaction mixture contains peroxides, carboxylic acids, or hydrochloric acid (301).

Sometimes addition of another ion can cause hydrogenation of the ethylene group to take place preferentially. Weygand and Werner (321) have recently shown that platinum black catalyzes the hydrogenation of the carbonyl group, the ethylene double bond, and the aryl nucleus of p-methylchalcone (I) in acetic acid solution.

I

p-Methylchalcone
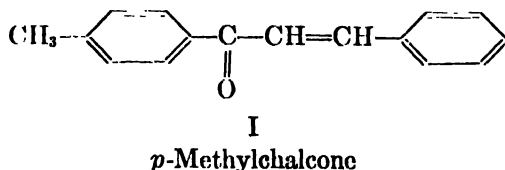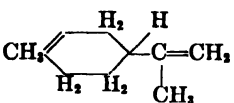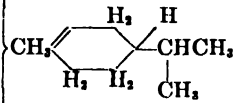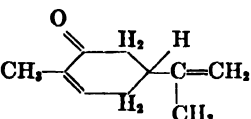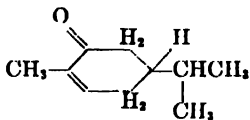
In aqueous solution, and with ferric chloride present in a definite concentration (0.0025 mole per 100 cc.), the reaction stopped abruptly with the addition of 2 moles of hydrogen, yielding the saturated alcohol:
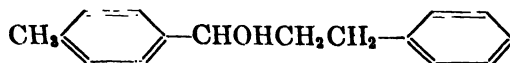
When the same concentration of ferric chloride was used in the hydrogenation *of stilbene and cinnamic acid, the reaction stopped abruptly with saturation of the ethylene group.*

The selective hydrogenation of an ethylene group conjugated with another will be discussed in section IV E. When there are two ethylene groups in a molecule, and they are not conjugated with each other, it is sometimes possible to obtain a consecutive hydrogenation, and to isolate the intermediate mono-

TABLE 19

Selective catalytic hydrogenation of non-conjugated diolefins

COMPOUND REDUCED	CATALYST	PRIMARY PRODUCT	REFER-ENCE
Limonene............................	CuO		(139)
	Ni-kie-selguhr		(15)
Citral............................. $CH_3C=CHCH_2CH_2C=CHCHO$ $\quad\quad\mid\quad\quad\quad\quad\mid$ $\quad\quad CH_3\quad\quad\quad\quad CH_3$	Ni-kie-selguhr	$CH_3C=CHCH_2CH_2CHCH_2CHO$ $\quad\quad\mid\quad\quad\quad\quad\quad\mid$ $\quad\quad CH_3\quad\quad\quad\quad\quad CH_3$	(15)
Geraniol........................ $CH_3C=CHCH_2CH_2C=CHCH_2OH$ $\quad\quad\mid\quad\quad\quad\quad\mid$ $\quad\quad CH_3\quad\quad\quad\quad CH_3$	Ni-kie-selguhr	$CH_3C=CHCH_2CH_2CHCH_2CH_2OH$ $\quad\quad\mid\quad\quad\quad\quad\quad\mid$ $\quad\quad CH_3\quad\quad\quad\quad\quad CH_3$	(15)
Linalool.. .... $\quad\quad\quad\quad OH$ $\quad\quad\quad\quad\mid$ $CH_3C=CHCH_2CH_2CCH=CH_2$ $\quad\quad\mid\quad\quad\quad\quad\mid$ $\quad\quad CH_3\quad\quad\quad\quad CH_3$	Ni-kie-selguhr	$\quad\quad\quad\quad OH$ $\quad\quad\quad\quad\mid$ $CH_3C=CHCH_2CH_2CCH_2CH_3$ $\quad\quad\mid\quad\quad\quad\quad\mid$ $\quad\quad CH_3\quad\quad\quad\quad CH_3$	(15)
Carvone.....	Ni-kie-selguhr		(15)
2-Ethyl-6-methyl-1,5-heptadiene.... $(CH_3)_2C=CHCH_2CH_2C=CH_2$ $\quad\quad\quad\quad\quad\quad\quad\mid$ $\quad\quad\quad\quad\quad\quad\quad C_2H_5$	Raney nickel	$(CH_3)_2C=CHCH_2CH_2CHCH_3$ $\quad\quad\quad\quad\quad\quad\quad\mid$ $\quad\quad\quad\quad\quad\quad\quad C_2H_5$	(76)

ölefins. In general, the double bond with the fewer substitutions is hydrogenated first. Some cases of such selective hydrogenation are given in table 19.

D. *Hydrogenation of acetylenes, and the stereochemical course of hydrogenation*

The acetylene bond is readily attacked by hydrogen in the presence of a catalyst, under mild conditions, and a wide variety of catalysts may be used. While very little attention has been paid to the effect of substituents on the ease of hydrogenation of the triple bond, there is some evidence to indicate that an

accumulation of phenyl groups hinders, and may completely inhibit, hydrogenation. Tetraphenylbutyndiol, $(C_6H_5)_2C(OH)C{\equiv}CC(OH)(C_6H_5)_2$, and 1,4-diphenyl-1,4-di-α-naphthylbutyndiol are hydrogenated much more slowly in the presence of colloidal palladium than are purely aliphatic acetylenic glycols of about the same molecular weight (345, 347, 352). Wieland and Kloss (324) found that di(triphenylmethylacetylene), $(C_6H_5)_3C{-}C{\equiv}C{-}C(C_6H_5)_3$ is not attacked by hydrogen in the presence of platinum or palladium catalysts, and that 1,3,3,3-tetraphenyl-1-propyne, $(C_6H_5)_3C{-}C{\equiv}C{-}C_6H_5$, is hydrogenated only very slowly.

Ordinarily, but few side reactions accompany the hydrogenation of acetylenes, especially when the reaction is carried out under mild conditions; occasionally polymerization occurs, and with tertiary acetylenic carbinols some cleavage of the molecule to a ketone may take place (293).

$$R_1{-}\underset{\underset{OH}{|}}{\overset{\overset{R_2}{|}}{C}}{-}C{\equiv}CH \;\longrightarrow\; R_1{-}\overset{\overset{R_2}{|}}{C}{=}O \;+\; HC{\equiv}CH$$
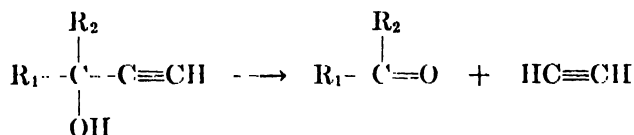
The two points of chief interest in the catalytic hydrogenation of acetylenes are the selectivity of the process, and, in the case of disubstituted acetylenes, the stereochemical course of the reaction. The hydrogenation of acetylene itself has been investigated mainly with a view towards developing a synthesis of ethylene and of liquid hydrocarbons suitable for use as motor fuels.

Acetylene can be reduced to ethylene or ethane in good yields over a variety of catalysts at low temperatures. At higher temperatures, considerable polymerization occurs. Since there is no sharp break in the hydrogenation curve at half-reduction, the relative amounts of ethylene and ethane obtained depend, to a large extent, on the proportions of hydrogen and acetylene used, and to a less extent on the temperature - ethane formation is favored at higher temperatures - and on the catalyst. Platinum catalysts tend to favor the formation of ethane (236, 259, 260), and it is easier to stop at the ethylene stage with palladium and nickel catalysts (1, 106, 219, 254, 259). Pilcher (240) found that at 55°C. with a nickel-molybdenum catalyst ethylene and ethane were produced. Ross, Culbertson, and Parsons (254) found that an 80 per cent yield of ethylene could be obtained by passing a mixture of 47 volume per cent acetylene and 53 volume per cent hydrogen over freshly reduced nickel.

Polymerization, which occurs to some extent even at low temperatures, predominates at higher temperatures, and the main reaction product consists of liquid, petroleum-like hydrocarbons. By suitable regulation of the temperature and the catalyst activity, it is possible to obtain liquid motor fuels of practically any desired boiling range (239, 282).

The course of the hydrogenation of substituted acetylenes depends to a great extent on the nature of the catalyst used, and to a less extent on the nature of the substituents. With platinum black the reaction is non-selective and non-uniform, and cannot be stopped at the olefin stage; at least, it is not possible to

obtain high yields of the olefin in this way, since apparently it starts to undergo hydrogenation almost as soon as it is formed (41, 72, 188, 345, 351, 356). Palladium black likewise does not bring about selective hydrogenation to the olefin (41, 356). With colloidal palladium, on the other hand, reduction is selective in the large majority of cases studied, and when one molar equivalent of hydrogen has been added, the product is largely or entirely the olefin (11, 42, 44, 45, 123, 161, 163, 197, 230, 280, 345, 350, 353). There is, apparently, but one general exception to this rule: Lai (181) was unable to obtain any selective hydrogenation of acetylenic bromides of the type $RC\equiv CCH_2Br$, and the triple bond was always saturated.

Bourguel (44) has pointed out that this selectivity is not due to the fact that the acetylenes are always reduced more rapidly than the corresponding olefins, for this is not the case. With monosubstituted acetylenes (44), arylacetylenes (45, 344, 356), acetylenic alcohols (346, 356), and some unsymmetrical acetylenic glycols (356), the olefins add hydrogen as rapidly as (or even more rapidly than) the acetylenes, yet even here the selectivity occurs. This selective action of colloidal palladium is very probably connected with selective adsorption of the acetylene on the catalyst, and little or no olefin can be adsorbed until the acetylene is used up (91). Ott and Schurmann (229) considered that the selectivity was connected with reaction velocity, and believed that those catalysts which gave the highest reaction velocity showed the least selective action; in view of the fact that the velocity of hydrogenation with colloidal palladium can be as great as that with platinum black, this explanation does not seem probable.

Raney nickel catalyst shows a selective action similar to that of colloidal palladium. Dupont (74) and Campbell and O'Connor (59) have shown that mono- and di-substituted acetylenes can be reduced smoothly to the corresponding olefins in the presence of this catalyst. This is also true for tertiary acetylenic carbinols (59). With monosubstituted alkylacetylenes, phenylacetylene, and phenylmethylacetylene there is no sharp break in the hydrogenation curve at the olefin stage, yet the olefin can be isolated in good yield. Dialkyl- and diaryl-acetylenes show a very sharp break in the curve at half-hydrogenation, as do the acetylenic carbinols (59).

Raney iron shows a selectivity more marked than that of Raney nickel, for in the cases of amyl-, hexyl-, and phenyl-acetylenes, and of some dialkylacetylenes, the reduction proceeds to the olefin stage and stops there (238, 302). This catalyst is much less active than Raney nickel and requires higher temperatures and pressures. Collodial platinum sometimes shows a selective action (325, 344), as do various palladium and nickel–charcoal catalysts (228) and reduced nickel (120, 197).

The stereochemical course of the hydrogenation of disubstituted acetylenes and certain olefins has been of considerable interest because of its connection with the mechanism of catalytic hydrogenation. Early work by Paal (230) and by Kelber and Schwartz (161) indicated that the hydrogenation of such substances as phenylpropiolic acid and tolane by hydrogen in the presence of colloidal palladium led to the pure *cis* olefins, whereas reduction by chemical meth-

ods formed the *trans* isomers. Later work, however, of Zalkind and his students on acetylenic glycols (345, 348, 351), of Williams and James (325) on acetylene-dicarboxylic acid and tolane, and of Ott and his coworkers (228, 229) on acetylenic acids and tolane, seemed to show that the reaction was not so simple, and that varying mixtures of *cis* and *trans* olefins were produced. Zalkind (345, 346) reported that in the hydrogenation of tetramethylbutyndiol, $(CH_3)_2$-$C(OH)C\equiv CC(OH)(CH_3)_2$, the more rapid the hydrogenation, the more of the *cis* olefin was formed, and he considered that the amount of catalyst used was important in determining the relative proportions of the *cis* and *trans* isomers formed. Ott and Schroeter (228) endeavored, by using poisoned catalysts, to establish a relationship between the activity of the catalyst and the relative amounts of *cis* and *trans* isomers obtained; although they had difficulty in obtaining reproducible results, they concluded that the more active catalysts gave larger amounts of the *cis* form. In the hydrogenation of tolane over a nickel- or palladium-charcoal catalyst, isostilbene was obtained, but when a cobalt-charcoal catalyst was used, some *trans*-stilbene was formed.

The more recent work of Bourguel (42, 44, 45), of Dupont (74), and of Campbell and Eby (56) on the catalytic hydrogenation of disubstituted acetylenes, and of Farkas and Farkas (89, 90, 91, 92), Greenhalgh and Polanyi (124), and others on the mechanism of catalytic hydrogenation and exchange reactions, has done much to clear up the confusion. Bourguel and his students (42, 44, 123) have shown that the olefin obtained by the hydrogenation of a disubstituted acetylene in the presence of colloidal palladium (on starch) is almost always the *cis* isomer, uncontaminated by any of the *trans* form; they established the configurations of many of the olefins by means of Raman spectra. The only case reported by Bourguel in which any *trans* olefin was obtained was that of 4-phenyl-3-butyn-2-one, $C_6H_5C\equiv CCOCH_3$ (42). Other workers (153, 253, 280) have used this method to prepare pure *cis* olefins, and have not reported the formation of any *trans* isomers. Campbell and Eby (56, 57) and Dupont (74) have found that this is true also for Raney nickel catalyst; the *cis* olefins can be obtained easily and in a state of purity by hydrogenating dialkylacetylenes in the presence of Raney nickel. The configurations of many of the olefins so obtained have been established by Raman spectra, dielectric-constant measurements, freezing-point data, etc.

Bourguel (42) has suggested that the *primary* product in any catalytic hydrogenation of a disubstituted acetylene is always the *cis* form of the olefin, and that this might undergo stereochemical conversion to the *trans* form in the presence of the hydrogenation catalyst. Such a conversion would be favored by a relatively slow hydrogenation velocity, and this would serve to explain the results of Zalkind and Ott mentioned above. Bourguel (42) has also pointed out that in those cases where some of the *trans* forms have been obtained by Zalkind and Ott, the *cis* forms of the olefins were relatively unstable and easily converted to their *trans* isomers--this is true of maleic acid, allocinnamic acid, and isostilbene--whereas when purely aliphatic olefins were produced, no *trans* forms were obtained. Aliphatic *cis* olefins are extremely resistant to conversion to the *trans* olefins by the usual means (61, 253).

From studies of the hydrogenation of ethylene and the catalytic exchange reaction between deuterium and ethylene, Farkas and Farkas (90) have proposed that low-temperature catalytic hydrogenation of an unsaturated linkage occurs by the *simultaneous* addition of two hydrogen atoms from the same hydrogen molecule, to the unsaturated bond, in contrast to chemical reduction, which probably occurs by a stepwise mechanism (see section II B). On this basis, catalytic hydrogenation of disubstituted acetylenes should always yield the *cis* olefins, *cis* ethylenic compounds should form the meso saturated derivatives, and *trans* ethylenic compounds the *racemic* saturated compounds, as primary hydrogenation products, whereas chemical reduction should yield the more stable form, *trans* or meso, as the case may be. The *cis* olefin formed from the acetylene could be subsequently converted to the *trans* by a catalytic exchange reaction, and the racemic saturated compound to the meso (the more stable form), either by enolization (if a carbonyl group is present) or by racemization. If the hydrogenation occurs rapidly enough, and if the product formed is relatively stable, the primary product would be the one isolated. This explains the non-appearance of any *trans* olefin in the catalytic hydrogenation of dialkylacetylenes over colloidal palladium or Raney nickel. If, on the other hand, the hydrogenation takes place relatively slowly, and the primary product is one which is easily converted to its stereoisomer, then mixtures might be expected; mixtures are found in the hydrogenation of tolane, acetylenedicarboxylic acid, and dimethylfumaric acid over comparatively inactive catalysts (227, 228, 229).
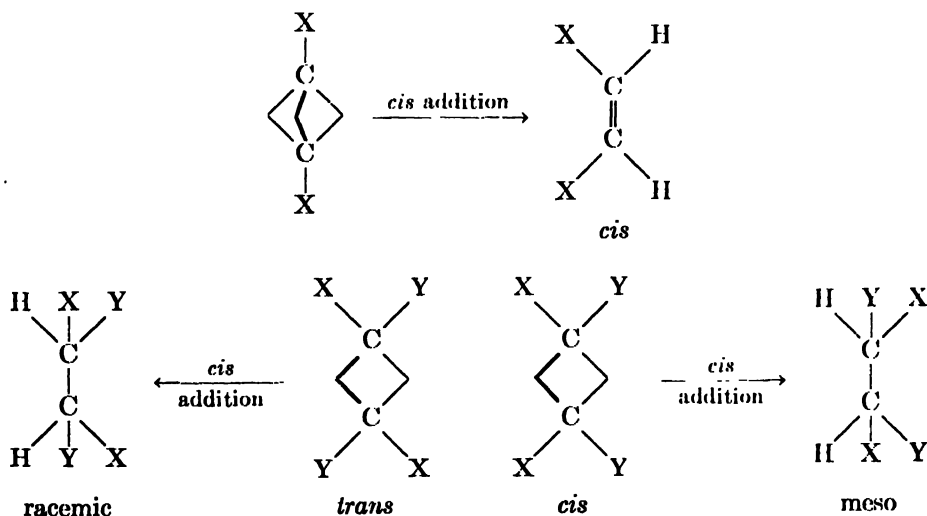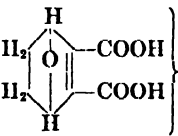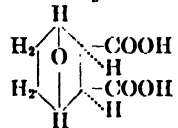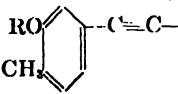
Wessely and Welleba (320a) have recently used catalytic hydrogenation to establish the configurations of diethylstilbestrol and its dimethyl ether. These substances, on treatment with hydrogen in the presence of palladium sponge, gave high yields of the racemic saturated derivatives, and therefore must have the *trans* structures.

The data on the stereochemical course of hydrogenation are summarized in table 20.

TABLE 20

Stereochemical course of hydrogenation of acetylenes and olefins

COMPOUND REDUCED	CATALYST AND CONDITIONS	CONFIGURATION OF PRODUCT	REFERENCES
2-Pentyne................	Pd–starch, room temperature	*cis*	(280)
	Pd–BaSO₄	*cis*	(163)
•	Colloidal Pd	*cis*	(123)
2-Hexyne........................	Colloidal Pd	*cis*	(123)
	Raney Ni	*cis*	(57)
3-Hexyne	Colloidal Pd	*cis*	(253)
	Raney Ni	*cis*	(57)
2-Heptyne......................	Colloidal Pd	*cis*	(123)
2-Octyne	Colloidal Pd	*cis*	(123)
	Raney Ni	*cis*	(57, 74)
3-Octyne......................	Raney Ni	*cis*	(56)
4-Octyne	Raney Ni	*cis*	(56)
5-Decyne.....................	Raney Ni	*cis*	(56)
Tetramethylbutyndiol............	Raney Fe	*cis*	(302)
(CH₃)₂CC≡CC(CH₃)₂ OH OH	Colloidal Pd, homogeneous solution	*cis*	(42, 147)
	Colloidal Pd in ethyl acetate	Some *trans*	(42)
	Colloidal Pd	Mixture of *cis* and *trans*	(346)
	Pd–charcoal	*cis*	(228)
	Poisoned catalysts	*cis* + 30% *trans*	(228)
1-Phenyl-1-propyne..............	Colloidal Pd	*cis*	(123)
Diphenylacetylene...............	Colloidal Pd, ethyl acetate	*cis*	(42)
	Colloidal Pd, acetic acid	*cis*, trace of *trans*	(161)
	Ni– or Pd–charcoal	*cis*	(228)
	Co–charcoal	*cis* + 8% *trans*	(228)
o,o'-Dinitrotolane................	Ni, neutral solution, cold	*cis*–Diaminostilbene	(256)
Tetraphenylbutyndiol............. (C₆H₅)₂CC≡CC(C₆H₅)₂ OH OH	Colloidal Pd	Various mixtures of *cis* and *trans*	(345)
1,4-Diphenyl-1,4-di-*p*-tolylbutyndiol...........................	Colloidal Pt	71% *cis*, 19% *trans*	(351)
1,4-Diphenyl-1,4-di-α-naphthylbutyndiol.....................	Colloidal Pd	96% *cis*, 4% *trans*	(352)
3-Phenyl-2-propyn-1-ol............ C₆H₅C≡CCH₂OH	Colloidal Pd	*cis*	(42)
Tetrolic acid...................... CH₃C≡CCOOH	Colloidal Pt	63% *cis*, 4% *trans*	(325)
	Colloidal Pd	*cis*	(42)
Ethylpropiolic acid.....	Colloidal Pd	*cis*	(42)
Propylpropiolic acid	Colloidal Pd	*cis*	(42)
Amylpropiolic acid......	Colloidal Pd	*cis*	(42)

TABLE 20—*Continued*

COMPOUND REDUCED	CATALYST AND CONDITIONS	CONFIGURATION OF PRODUCT	REFER-ENCES
Hexylpropiolic acid...............	Colloidal Pd	*cis*	(42)
Stearolic acid....................... $CH_3(CH_2)_7C\equiv C(CH_2)_7COOH$	Reduced Ni	*cis* (oleic)	(120)
Behenolic acid.................... $CH_3(CH_2)_7C\equiv C(CH_2)_{11}COOH$	Reduced Ni	*cis* (erucic)	(120)
Acetylenedicarboxylic acid...... ..	Colloidal Pt (K salt)	*trans*	(325)
	Colloidal Pd	*cis*	(42)
	Colloidal Pd, poisons	Chiefly *cis*, some *trans*	(228)
Phenylpropiolic acid...............	Colloidal Pd	*cis*	(42, 230)
.... $C_6H_5C\equiv CCOCH_3$	Colloidal Pd	....	(..)
cis-Dimethylstilbene..............	Pd-charcoal	90% meso, 10% racemic	(227)
	Pd sponge, acetic acid	99% meso	(320a)
trans-Dimethylstilbene............	Pd-charcoal	Racemic	(227)
	Pd sponge, acetic acid	98% racemic	(320a)
Dimethylmaleic acid..............	Pd or Ni-charcoal	86% meso, 14% racemic	(227)
Dimethylfumaric acid......	Pd-charcoal	70% racemic, 30% meso	(227)
	Ni-charcoal	Racemic only	(227) (9)
	Pt black		
	Colloidal Pd	*cis*	(132a)
Diethylstilbestrol................. $HOC_6H_4C\!=\!CC_6H_4OH$ $\quad\mid\quad\mid$ $H_5C_2\ C_2H_5$	Pd sponge, acetic acid	88% racemic saturated	(320a)
Diethylstilbestrol dimethyl ether..	Pd sponge, acetic acid	97% racemic saturated	(320a)

E. *Hydrogenation of conjugated systems*

Compounds containing conjugated systems of double bonds are, in general, fairly easily reduced by catalytic methods, and the point of chief interest in connection with this reaction has been to determine the mode of addition of the hydrogen. It was long believed that catalytic hydrogenation of such systems, in contrast to reduction by chemical methods, occurred by direct addition of molecular hydrogen to one or both of the unsaturated linkages, and that 1,4-addition did not take place. More recent work has shown, however, that

hydrogen can be added at the ends of the conjugated system by catalytic methods, and that this is true both for carbon–oxygen and for carbon–carbon conjugations. In the former case, by using compounds which would yield stable enols, it was possible to isolate these, and thus to demonstrate that terminal addition of hydrogen had taken place, to some extent at least.

Kohler and Thompson (170, 170a) found that hydrogenation of β-phenyl-benzalacetomesitylene in the presence of palladium–calcium carbonate catalyst yielded 88 per cent of the saturated ketone, and 12 per cent of its enol, which is relatively stable under the conditions used. Hence, 1,4-addition of hydrogen occurred to the extent of at least 12 per cent.

$$(C_6H_5)_2C{=}CHCC_6H_2(CH_3)_3 \xrightarrow{\text{catalyst, H}_2} (C_6H_5)_2CHCH{=}CC_6H_2(CH_3)_3$$
$$\underset{O}{\|} \qquad\qquad\qquad\qquad\qquad \underset{OH}{|}$$
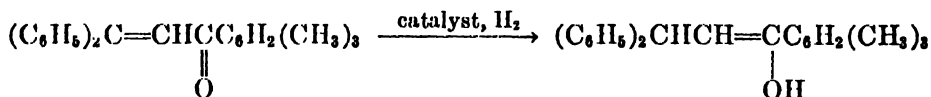
In an analogous manner, using mesityl-substituted unsaturated 1,4-diketones, Lutz and Reveley (203) showed that a large amount of terminal addition of hydrogen occurred, for iodine titration showed the presence of as high as 90 per cent of the dienol in some cases.

$$(CH_3)_3C_6H_2CCH{=}CHCC_6H_2(CH_3)_3 \longrightarrow$$
$$\underset{O}{\|} \qquad\quad \underset{O}{\|}$$

$$(CH_3)_3C_6H_2C{=}CHCH{=}CC_6H_2(CH_3)_3$$
$$\underset{OH}{|} \qquad\qquad \underset{OH}{|}$$
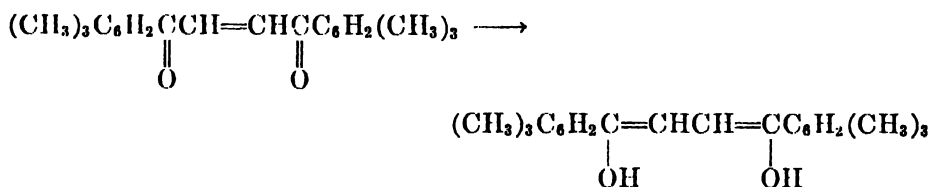
The amount of dienol (and therefore the amount of 1,6-addition of hydrogen) depends to a considerable extent on the temperature and the solvent used in the hydrogenation; at 0°C. more dienol was found than at 30°C., and more 1,6-hydrogenation occurred in ethyl alcohol (94 per cent) than in decalin (17 per cent). The catalytic hydrogenation of benzalacetone under reduced pressure has been shown by Grignard to give at least 22 per cent of the enol, that is, of 1,4-addition (125).

In the hydrogenation of compounds containing carbon–carbon conjugation, there is a strong tendency for both double bonds to be hydrogenated at about the same rate. Hence, at half-hydrogenation the reaction product may contain considerable amounts of unreacted diene and of the fully saturated compound, together with some of the possible dihydro products. Under these conditions, analysis of the mixture is complicated, and it is possible that in many cases the presence of small amounts of dihydro compounds has been overlooked, and that the structures of those found have been misinterpreted. In early work, which was carried out on rather complicated molecules such as cinnamalcamphor and cinnamalmalonic ester, it was reported that at half-hydrogenation no dihydro products were present, but solely an equimolar mixture of the original diene and its saturated derivative (231). More recent work has shown, however, that

stepwise hydrogenation does occur, to some extent, in many cases and that, occasionally at least, terminal addition of hydrogen takes place. The nature of the catalyst is important in determining whether any dihydro compounds will be present at half-hydrogenation; for this purpose platinum catalysts are less satisfactory than Raney nickel (78, 99) or palladium (98). It will be noticed that the catalysts which give the most selective hydrogenation of a conjugated system are the same ones that show greatest selectivity in the hydrogenation of acetylenes to olefins.

Lebedev and Yakubchik (189, 190) found that in the hydrogenation of purely aliphatic diene hydrocarbons over platinum black, dihydro compounds could be isolated at half-reduction. With some types, such as 2,5-dimethyl-2,4-hexadiene, $(CH_3)_2C$=CHCH=C($CH_3)_2$, a definite break occurred in the hydrogenation curve at half-hydrogenation, and when the reaction was stopped at this point, the 1,4-dihydro product was isolated. With other dienes, among them butadiene, piperylene, and isoprene, addition of hydrogen occurred in all possible ways, and although there were several breaks in the curves, none of them corresponded to the half-hydrogenation point. When the hydrogenation of isoprene was stopped at the addition of one equivalent of hydrogen, the reaction mixture was found to contain 30 per cent of the saturated hydrocarbon and 30 per cent of unattacked isoprene, together with 12 to 15 per cent of each of the possible dihydro derivatives.[3] Muskat and Knapp (221) were able to isolate the 3,1-dihydro compound when phenylbutadiene was hydrogenated in the presence of platinum black, but Kuhn and Winterstein (177) could obtain no partially hydrogenated products from the α,ω-diphenylpolyenes with this catalyst.

Raney nickel gives more stepwise hydrogenation than does platinum black. Dupont and Pacquot (78) have shown by means of Raman spectra that the product isolated from the half-hydrogenation of isoprene over Raney nickel is an approximately equimolar mixture of the 1,4- and 3,4-dihydro compounds, 2-methyl-2-butene and 2-methyl-1-butene; no 1,2-dihydro compound, 2-methyl-3-butene, was obtained. The hydrogenation of β-myrcene is of considerable interest (see page 154). When it is hydrogenated over Raney nickel or palladium–charcoal, the main product is that formed by 1,4-addition of hydrogen to the conjugatedsystem (I); some of the 1,2-dihydro compound is also obtained (II), but in neither case is any 3,4-dihydro compound formed, nor is the isolated double bond attacked. When the catalyst is platinum oxide platinum black, the reaction does not stop with addition of 1 mole of hydrogen, and the first product isolated is the monoölefin (III), in which only the highly substituted double bond remains unattacked. Sodium in alcohol yields I, mainly (75, 76).

Alloöcimene, in which there are three double bonds in conjugation, gives no homogeneous product when the reaction is stopped at the addition of 1 mole of hydrogen, but with 2 moles the product is largely 3,7-dimethyl-3-octene (IV),

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[3] These figures cannot be considered as accurate, for the method of analysis involved long contact (several months) with liquid sulfur dioxide, and some rearrangement probably occurred.

together with a little 3,7-dimethyl-2-octene (4); hence 1,4-addition of hydrogen must have occurred at some stage.

$$CH_3CH=CCH_2CH_2C=C(CH_3)_2$$
$$\qquad\quad | \qquad\qquad |$$
$$\qquad\quad CH_3 \qquad\quad H$$
$$\qquad\qquad\qquad\qquad I$$

$$CH_2=CH-C-CH_2CH_2CH=C(CH_3)_2 \rightarrow CH_3CH_2CCH_2CH_2CH=C(CH_3)_2$$
$$\qquad\quad \|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \|$$
$$\qquad\quad CH_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad II$$

$$CH_3CH_2CHCH_2CH_2CH=C(CH_3)_2$$
$$\qquad\qquad |$$
$$\qquad\qquad CH_3$$
$$\qquad\qquad\qquad III$$

$$(CH_3)_2CHCH_2CH_2CH=CCH_2CH_3$$
$$\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad CH_3$$

$$(CH_3)_2C=CH-CH=CH-C=CHCH_3 \qquad\qquad IV$$
$$\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad CH_3$$
$$\qquad\qquad\qquad (CH_3)_2CHCH_2CH_2CH_2C=CHCH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad V$$
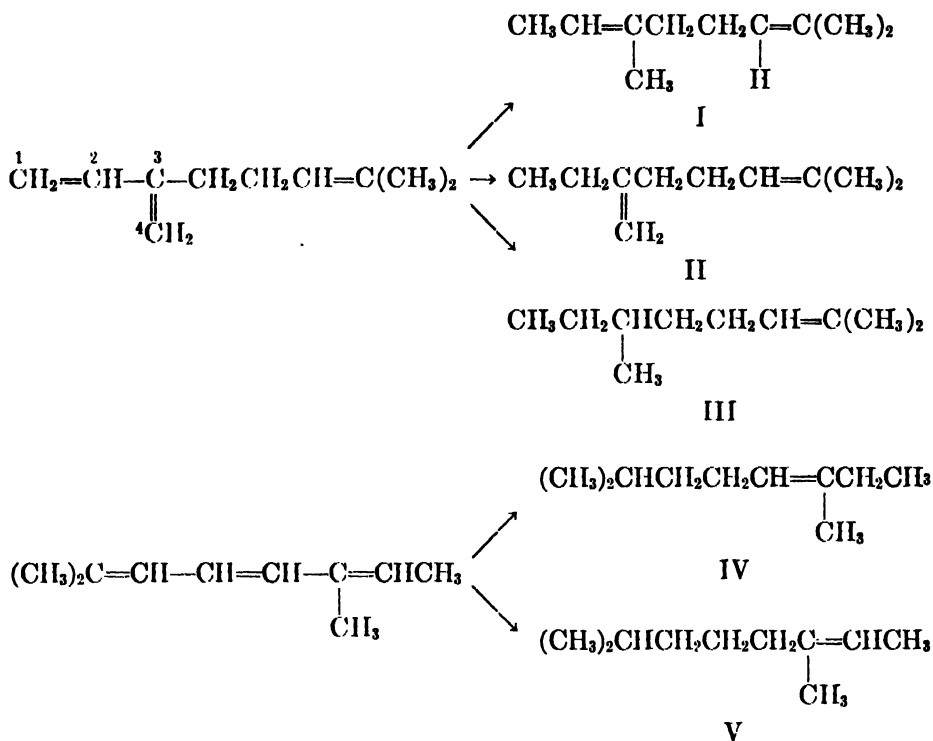
The hydrogenation of higher polyunsaturated acids, in which the carboxyl group is removed from the conjugation, has also been shown to go in a stepwise fashion, at least to some extent. Hydrogenation of 9,11-linoleic acid in the presence of reduced nickel yields some Δ^{10}-elaidic acid, and some partial hydrogenation of eleostearic acid occurred in the presence of this catalyst also (40).

When two or more ethylenic groups are in extended conjugation with a carbonyl group, as in vinylacrylic acid, sorbic acid, etc., the results recorded are contradictory. Several workers (137, 231) have reported that the saturation of both double bonds in these compounds takes place simultaneously when platinum black is used, and that no dihydro products can be isolated. On the other hand, Farmer and his coworkers, who also used platinum black as catalyst, were able to isolate dihydro compounds from vinylacrylic acid (94), sorbic acid (94, 95, 97, 98, 99), and some of the methylsorbic acids (94), as well as muconic acid (97), although the bulk of the product in each case consisted of unreduced acid and the saturated derivative. Isaacs and Wilson (144, 145, 146) also obtained dihydro derivatives from sorbic acid, as did Muskat and Knapp (221) from vinylacrylic acid, and Lebedev and Yakubchik (191) from piperic acid with the Adams catalyst. It is difficult to account for these discrepancies when the same type

of catalyst was used by different workers. A part of the trouble may be found in the difficulties of analyzing the mixtures, and another source of error may be in the age of the catalyst, as Farmer and Galley (95) found that a sample of the Adams catalyst which had been used once or twice gave a larger proportion of stepwise hydrogenation than did a fresh sample.

As with the diene hydrocarbons, palladium and Raney nickel catalysts have more tendency than platinum to bring about a stepwise hydrogenation of diene acids. This is shown in table 21, taken from the work of Farmer and Hughes (98).

The addition of hydrogen in the presence of these catalysts to the system

$$\overset{4}{C}=\overset{3}{C}-\overset{2}{C}=\overset{1}{C}-COOH$$ tends to occur in the 3,4-positions, although some 1,1-addition is also obtained. This stands in contrast to the results of reduction by alkali amalgams, in which 1,2- and 1,4-additions of hydrogen occur, but no 3,4-addition.

When an acetylenic bond is in conjugation with an ethylenic bond, it is frequently possible to obtain selective hydrogenation of the former, with the forma-

TABLE 21

Effect of catalysts on the hydrogenation of sorbic acid (98)

CATALYST	SORBIC ACID AT HALF-REDUCTION	SATURATED ACID AT HALF REDUCTION	DIHYDRO COMPOUNDS
	per cent	*per cent*	*per cent*
Raney nickel	4	4	83
Platinum black	44	44	12
Palladium oxide			88
Palladium–barium sulfate			90

tion of the corresponding diene. Palladium catalysts seem to be especially effective for this, but nickel ones may sometimes be used (55). Vinylacetylene with palladium catalysts yields butadiene, together with some butene and polymers (133, 134), whereas the reaction is entirely unselective when platinum black is the catalyst (192), and nickel–alumina catalyzes the formation of the saturated compound directly (192).

Raney iron can be used to convert a substituted vinylacetylene to the butadiene derivative; Thompson and Wyatt (302) found that 2-methyl-1-buten-3-yne, $CH_2=C(CH_3)C\equiv CH$, was thereby reduced to isoprene, and the reaction stopped at this point.

Very little work has been reported on the partial hydrogenation of hydrocarbons with crossed conjugated systems. Dialkylfulvenes, which undergo 1,4-reduction by chemical methods, on catalytic hydrogenation over palladium or platinum show no sharp breaks in the hydrogenation curve, and yield no partially hydrogenated products (153).

In the hydrogenation of diphenylfulvene, addition of the first mole of hydrogen

is non-selective, to the ring, but when palladium is the catalyst, a tetrahydro compound can be isolated (158).

$$
\begin{array}{ccc}
CH=CH & & CH_2CH_2 \\
| \quad \diagdown & & | \quad \diagdown \\
\quad \quad C=C(C_6H_5)_2 & \xrightarrow{2H_2} & \quad \quad C=C(C_6H_5)_2 \\
| \quad \diagup & & | \quad \diagup \\
CH=CH & & CH_2CH_2
\end{array}
$$

<center>Diphenylfulvene</center>
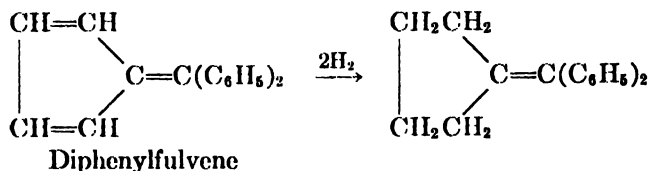
With divinylacetylenes, the triene stage cannot be isolated. When platinum catalysts are used, the reaction is entirely unselective, and continues to the saturated derivative; with palladium catalysts a monoölefin can sometimes be isolated (354, 355).

$$
\begin{array}{cc}
CH_2=CC\equiv CC=CH_2 & \cdots \rightarrow \quad CH_3CHCH_2CH_2-C=CH_2 \\
\quad | \quad \quad | & \quad \quad \quad | \quad \quad \quad \quad \quad | \\
\quad CH_3 \quad CH_3 & \quad \quad \quad CH_3 \quad \quad \quad \quad CH_3
\end{array}
$$
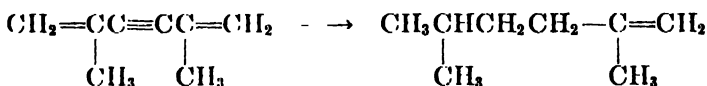
Blomquist and Marvel (37) were, however, unable to find any selective hydrogenation of 4,7-dipropyl-3,7-decadien-5-yne, $CH_3CH_2CH=C(C_3H_7)C\equiv CC-(C_3H_7)=CHCH_2CH_3$.

Very little work has been reported on the course of the hydrogenation of conjugated diacetylenes. Grignard and Tcheoufaki (126) have found that both 1,4- and 1,2-addition of hydrogen occurs with diphenyldiacetylene in the presence of platinum black, for they isolated diphenylbutatriene, diphenylbutadiene, and diphenylacetylene.

The results on the partial hydrogenation of conjugated hydrocarbons and diene acids are compiled in table 22.

F. Hydrogenation of aromatic hydrocarbons

The catalytic addition of hydrogen to the double bonds of an aromatic ring is much more difficult than it is to open-chain unsaturated linkages, and therefore requires more strenuous conditions of temperature and pressure, or a longer reaction time. Nevertheless, there is a wide variety of catalysts which will bring about the hydrogenation of aromatic systems, and the reaction is one of considerable commercial importance. For a complete discussion of the subject, the reader is referred to the books of Ellis (84), Adkins (4), Ipatieff (139), Berkman, Morrell, and Egloff (34) and others.

1. Hydrogenation of benzene and its derivatives

Benzene and its homologs can be reduced to the cyclohexane derivatives in the presence of platinum black catalysts, at pressures of 1 to 4 atm. and at or near room temperature; the reaction proceeds best in acetic acid solution (3, 327), or in the presence of a small amount of hydrogen halide acid (52), the acid seeming to exert a specific promoting effect. The hydrogenation is inhibited by sodium hydroxide (109). Willstätter and Waldschmidt-Leitz (331) have shown that the presence of oxygen in a platinum black catalyst is essential, but this is not true for colloidal platinum and palladium catalysts (284). Colloidal platinum

TABLE 22
Partial hydrogenation of conjugated compounds

COMPOUND REDUCED	CATALYST	PRODUCTS OF PARTIAL HYDROGENATION	REFERENCES
Isoprene............................ $$\overset{4}{CH_2}=\overset{3}{CH}\overset{2}{C}=\overset{1}{CH_2}$$ $$\|$$ $$CH_3$$	Raney Ni Pt oxide	50% 1,4- and 50% 3,4-dihydro 30% saturated; 12–15% of each possible dihydro compound	(78) (189, 190)
Dimethylbutadiene.................. $$\overset{1}{CH_2}=\overset{2}{C}-\overset{3}{C}=\overset{4}{CH_2}$$ $$\| \quad \|$$ $$H_3C \quad CH_3$$	Raney Ni	63% 1,2-dihydro; 37% 1,4-dihydro	(78)
β-Myrcene......................... $$\overset{1}{CH_2}=\overset{2}{CH}\overset{3}{C}CH_2CH_2C=C(CH_3)_2$$ $$\|$$ $$CH_2$$	Raney Ni Pt oxide Palladium	63% 1,4-dihydro; 37% 1,2-dihydro No dihydro; 3,7-dimethyl-6-octene 75% 1,4-dihydro; 25% 1,2-dihydro	(76) (76) (76)
Alloöcimene....................... $$\overset{1}{(CH_3)_2}\overset{2}{C}=\overset{3}{CH}\overset{4}{CH}=\overset{5}{CH}\overset{6}{C}=CHCH_3$$ $$\|$$ $$CH_3$$	Raney Ni Pt oxide	1,2,3,6-Tetrahydro; some 1,2,3,4-tetrahydro Same as given by Raney nickel	(77) (77)
1-Phenylbutadiene................. $$\overset{1}{C_6H_5}\overset{2}{CH}=\overset{3}{CH}\overset{4}{CH}=CH_2$$	Pt oxide	3,4-Dihydro	(221)
2,3-Diphenylbutadiene............. $$\overset{1}{CH_2}=\overset{2}{C}-\overset{3}{C}=\overset{4}{CH_2}$$ $$\| \quad \|$$ $$C_6H_5 \quad C_6H_5$$	Pt oxide	Non-selective	(12)
1,2,3,4-Tetraphenylbutadiene........	Pt oxide	Not reduced	(43)
α,ω-Diphenylpolyenes.............. $$C_6H_5(CH=CH)_nC_6H_5$$	Pt oxide	Non-selective	(177)
1,1,6,6-Tetraphenyl-1,3,5-hexatriene	Pt oxide	Non-selective	(331)
9,11-Linoleic acid...................	Ni, 180°C.	Δ^{10}-*cis*-Elaidic acid	(40)
Vinylacrylic acid................... $$\overset{4}{CH_2}=\overset{3}{CH}\overset{2}{CH}=\overset{1}{CH}COOH$$	Pt oxide Pt oxide	Non-selective 3,4-Dihydro 28% 3,4-dihydro; 8% 1,2-dihydro; 32% saturated compound	(137) (221) (94)
Sorbic acid $$\overset{4}{CH_3}\overset{3}{CH}=\overset{2}{CH}\overset{}{CH}=\overset{1}{CH}COOH$$	Pt oxide Pt oxide Pt oxide Pd–BaSO_4 Raney Ni	7% 3,4-dihydro; 44% of saturated compound Non-selective 31% 3,4-dihydro; 63% saturated 90% 3,4-dihydro 83–86% 3,4-dihydro	(94, 97) (137) (144, 332) (98) (98, 332)

TABLE 22—*Continued*

COMPOUND REDUCED	CATALYST	PRODUCTS OF PARTIAL HYDROGENATION	REFER-ENCES
α-Methylsorbic acid.................. .... $\overset{4}{C}H_3\overset{3}{C}H=\overset{2}{C}HCH=\overset{1}{C}COOH$ $\mid$ CH_3	Pt oxide	21% 3,4-dihydro; 26% 1,4-dihydro	(94)
β-Methylsorbic acid................. $\overset{4}{C}H_3\overset{3}{C}H=\overset{2}{C}HC=\overset{1}{C}HCOOH$ $\mid$ CH_3	Pt oxide	34% 3,4-dihydro; 14% 1,4-dihydro	(94)
Muconic acid.	Pt oxide	Non-selective	(137)
$\overset{1}{H}OOC\overset{2}{C}H=\overset{3}{C}HCH=\overset{4}{C}HCOOH$	Pt oxide	11% 3,4- and 7% 1,4-dihydro; 40% saturated	(97)
Piperic acid . . . . $CH_2O_2C_6H_4CH=CHCH=CHCOOH$	Pt oxide	33% dihydro	(191)
	Colloidal Pd	Non-selective	(231)
	Colloidal Pd	50% dihydro	(191)
Methysticin...... ... . $ArCH=\overset{3}{C}HCH=\overset{1}{C}HCOCH_2COOH$	Pd (on sodium salt)	1,2-Dihydro	(115)
	Pd (on methyl ester)	3,4-Dihydro	(115)
Vinylacetylene...................... $CH_2=CHC\equiv CH$	Palladium	1,3-Butadiene in good yields (60–80%)	(133, 134, 192)
	Platinum	Non-selective	(192)
Methylvinylacetylene.. .... $\overset{1}{H}C\equiv\overset{2}{C}-\overset{3}{C}=\overset{4}{C}H_2$ $\mid$ CH_3	Raney Fe	1,2-Dihydro (isoprene)	(302)
$\overset{1}{C}H_3\overset{2}{C}HC\equiv\overset{3}{C}CH=\overset{4}{C}H_2$ .... $\mid$ OH	Platinum	Non-selective	(355)
	Palladium	1,2-Dihydro	(366)
CH_3 $\mid\overset{1}{}\;\overset{2}{}\overset{3}{}\;\;\overset{4}{}$ $C_3H_7CC\equiv CCH=CH_2$............... $\mid$ OH	Palladium	1,2-Dihydro	(366)
CH_3 $\mid\overset{1}{}\;\overset{2}{}\overset{3}{}\;\;\overset{4}{}$ $C_2H_5CC\equiv CCH=CH_2$............... $\mid$ OH	Palladium	1,2-Dihydro	(349)
$\overset{1}{C}_6H_5\overset{2}{C}\equiv\overset{3}{C}CH=\overset{4}{C}(COOH)_2$............	Pd, pyridine	1,2-Dihydro (*cis-cis*)	(198)
Diphenyldiacetylene................. $\overset{1}{C}_6H_5\overset{2}{C}\equiv\overset{3}{C}C\equiv\overset{4}{C}C_6H_5$	Colloidal Pd	1,2,3,4-Tetrahydro: 25% *cis-cis*, 75% *cis-trans*	(161)
	Pd–charcoal	90% *cis-trans*-1,2,3,4-tetrahydro	(228)
	Ni–charcoal	33% *cis-cis* tetrahydro	(228)

TABLE 22—*Concluded*

COMPOUND REDUCED	CATALYST	PRODUCTS OF PARTIAL HYDROGENATION	REFER- ENCES
Divinylacetylene...................... $CH_2=CHC=CCH=CH_2$	Ni, 35°C.	3-Hexene	(55)
$CH_2=CC=CC=CH_2$................ | | CH_3 CH_3	Colloidal Pd	Mainly 2,5-dimethyl-1-hexene	(355)
$C_2H_5CH=CC=C—C=CHC_2H_5$...... | | C_3H_7 C_3H_7	Pt oxide	Non-selective	(37)
$RC=CC=CC=CR$................. | | R R	Ni	$RCH_2CHCH=CHCHCH_2R$ | | R R	(127)

(224) and palladium catalysts (286), nickel black (304), and osmium-asbestos (359) will also bring about the hydrogenation of benzene under mild conditions.

Reduced nickel is an effective catalyst, either for use with the Sabatier–Senderens technique at 180°C. (261), or for liquid-phase hydrogenation at higher temperatures and pressures of about 80 atm. (225); Raney nickel (4, 6), nickel–kieselguhr (5), and nickel–alumina catalysts (83) may also be used at temperatures varying from 100° to 175°C. and pressures of 30 to 170 atm. Nickel oxide catalysts can be used at higher temperatures and pressures (139). Reduced copper is not an efficient catalyst for the hydrogenation of benzene unless it contains traces of nickel (141), and copper chromite, except in a few rare cases, is not a satisfactory catalyst for the hydrogenation of aromatic nuclei (357).   With practically all of these catalysts the presence of small amounts of impurities in the compound being hydrogenated—especially sulfur-containing impurities—inhibits the reaction; recently sulfur-containing catalysts, such as the molybdenum sulfides, have been developed which are much less sensitive to poisoning, but these catalysts require very high temperatures (in the neighborhood of 400°C.) to be effective.

The hydrogenation of benzene and of its alkyl derivatives cannot be stopped at any intermediate stage, but proceeds directly to the cyclohexane, which may or may not undergo secondary reactions, depending on the conditions.   This does not prove, however, that the hydrogenation is not a stepwise one, for it is possible that the intermediate compounds, being cyclic dienes or olefins, are hydrogenated more readily than the original aromatic compound, and are formed, but are immediately hydrogenated.   Some evidence for a stepwise course has been presented by Truffault (305), who found that when benzene is hydrogenated over nickel in the presence of phosphorus pentoxide as inhibitor, cyclohexylbenzene is obtained; he considered that a condensation occurred between benzene and a partially hydrogenated product to form this substance.

The hydrogenation of phenols has definitely been shown to take a stepwise course; Vavon and his students (311, 312) found that cyclohexanone is an intermediate in the hydrogenation of phenol to cyclohexanol, and Grignard was

able, by working at pressures of 18 to 22 mm., to isolate the enol of cyclohexanone and to establish the course of the reaction as follows:

Phenol   Cyclohexanol

Cyclohexanone
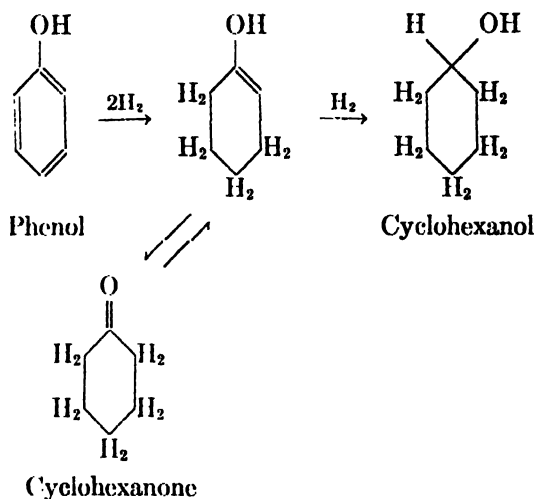
The effect of substituents in the benzene ring on the ease of hydrogenation of the nucleus is by no means clear-cut, and contradictory results have been reported. Phenols seem to undergo hydrogenation more easily than do the hydrocarbons over nickel and platinum (4, 50, 71, 200a, 314); etherification of the hydroxyl group removes this effect. Amine groups retard the hydrogenation (71, 200a), as do carbethoxy groups (4); Willstätter and Hatt (327), however, found that benzoic acid was hydrogenated more easily than benzene in the presence of platinum black. Considerable confusion exists as to the effect of alkyl groups. Willstätter and Hatt (327), using platinum black, found that toluene and durene were hydrogenated more easily than benzene; Altman (13) has obtained similar results for a molybdenum sulfide catalyst. On the other hand, several workers have reported that alkyl groups decrease the ease of hydrogenation of the benzene ring in the presence of nickel–alumina (82), nickel black (305), palladium (8), and platinum catalysts (224). Lozovoi and Dyakova (199), using nickel on alumina, found that the size of the side chain, in varying from C_1 to C_8, had little effect on the ease of hydrogenation, but that the number of side chains had a marked effect (200). They obtained the relative reactivities recorded in table 23.

Some work has been done on the stereochemical configuration of the products obtained from the hydrogenation of disubstituted benzenes, but the results are somewhat confusing. The hydrogenation of the xylenes in the presence of colloidal platinum in acetic acid solution, according to Skita (285), yields a mixture of the cis- and trans-dimethylcyclohexanes, whereas cymene gives the cis saturated compound. Adams and Marshall (3), on the other hand, using the Adams catalyst and acetic acid as solvent, obtained only the trans-dimethyl-

cyclohexane from *m*-xylene. Zelinsky and Margolis (360) and Margolis (206) have found that *o*- and *p*-xylenes on treatment with hydrogen at 50 70°C. in the presence of osmium–asbestos are converted to the *cis*-dimethylcyclohexanes; if the Sabatier-Senderens procedure is used, with reduced nickel, at 170 -180°C., the *trans* isomers are obtained. Since the *cis* compound is converted to the *trans* by passage over nickel at 170°C., but the *trans* is not changed to the *cis* in the presence of osmium at 70°C., it is probable that the primary product in both cases is the *cis* form, and that this may or may not rearrange to the *trans*, depending on the conditions.
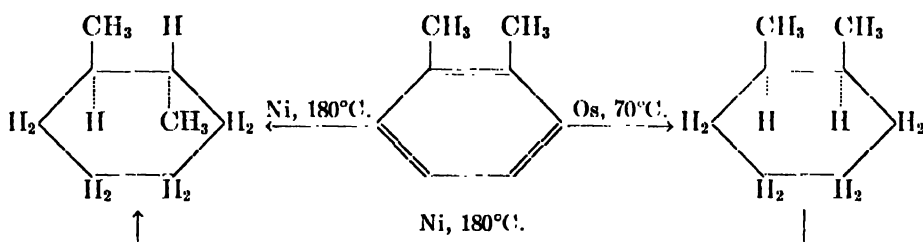
Hydrogenation of alkylphenols over platinum catalysts, in acetic acid solution, yields either the *cis*-alkylcyclohexanol, or a mixture of the *cis* and *trans* forms,

TABLE 23

Relative reactivities in hydrogenations over nickel–alumina (200)

COMPOUND	RELATIVE REACTIVITY	COMPOUND	RELATIVE REACTIVITY
Styrene	900	Benzene	1
1-Hexene	306	Toluene	0.4
Cyclopentene	294	Xylene	0.22
Cyclohexene	150	Trimethylbenzene	0.1
1-Methyl-3-cyclohexene	134	Tetramethylbenzene	0.04
1-Methyl-1-cyclohexene	5	Pentamethylbenzene	0.005
Naphthalene	3.3	Hexamethylbenzene	0.001

with the former predominating (283, 311, 313). At higher temperatures, over a nickel catalyst, the *trans* form may be obtained (20).

In the hydrogenation of benzene derivatives, the cyclohexane is usually formed in good yield, and without large amounts of side reactions. In some cases, however, hydrogenolysis may occur, or the reaction product may undergo secondary reactions. Adkins (4, 357) observed that phenol ethers, benzyl alcohol, and pentaphenylethane undergo some hydrogenolysis, with the formation of cyclohexane, toluene, and tri- and di-cyclohexylmethanes, respectively. When benzene is hydrogenated at high temperatures, the cyclohexane formed is partially changed to methylcyclopentane, and other deep-seated changes may occur. Thus, using nickel oxide at 460°C. (272), or molybdenum sulfide at 430°C.

(14, 249, 250), methyl cyclopentane is obtained, and in some cases hexane, methane, toluene, and cyclopentane have been isolated (225). Alkylbenzenes may undergo migration or cleavage of the alkyl groups; toluene at 400°C. over molybdenum sulfide yields methylcyclohexane, dimethylcyclopentane, cyclopentane, etc.

In contrast to the simple benzene derivatives, the polynuclear hydrocarbons are hydrogenated stepwise, and the intermediate steps can frequently be isolated. Hydrogenation of many of these hydrocarbons is easier than that of benzene, owing to the more aliphatic nature of some of the double bonds.

2. Hydrogenation of naphthalene

Naphthalene can be hydrogenated to tetralin or decalin, depending on the conditions. In contrast to reduction by chemical methods, no dihydronaphthalene can be isolated from the catalytic hydrogenation (255). In some cases tetralin is definitely an intermediate in the formation of decalin; in others the decalin appears to be formed directly. Willstätter and Seitz (329) have found that a platinum catalyst rich in oxygen causes the formation of tetralin at room temperature; if the catalyst is poor in oxygen, decalin is formed directly, and no tetralin can be detected. The decalin so obtained has been shown to be the *cis* form (330). Maillard (201) has shown that hydrogenation of naphthalene at 20°C. with active nickel also leads to the direct formation of decalin; above 60°C., however, the reaction is stepwise, and tetralin can be isolated.
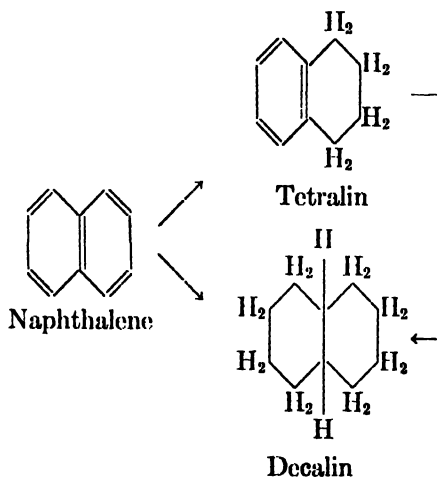
In many cases, both tetralin and decalin are formed; in others, either compound can be obtained by changing the temperature and pressure. Table 24 contains a summary of some of the work in this field.

If the temperature is too high, the tetralin and decalin formed may undergo decomposition to yield benzene derivatives. Reduced nickel at 460–500°C. causes the formation of some of these (225), as do nickel and iron oxide catalysts

above 450°C. (140), molybdenum sulfide above 360°C. (245), and molybdenum oxide at 435°C. (81).

Sodium and sodium hydride, which do not catalyze the addition of hydrogen to benzene, are effective catalysts for the hydrogenation of naphthalene (33a, 128, 131, 132), and for other compounds which are capable of adding sodium, such as styrene. These catalysts are most effective at temperature of about

TABLE 24

Catalytic hydrogenation of naphthalene

CATALYST	TEMPERA-TURE	PRESSURE	MAIN PRODUCT	REFERENCES
	°C.			
Reduced Cu	200	80 atm.	Tetralin	(171)
Reduced Cu	260	80 atm.	Decalin	(171)
Pt black	Room	Atmospheric	Decalin	(329)
Osmium–asbestos	90–160	Atmospheric	Decalin	(359)
NiO, CuO, Fe₂O₃	450		Tetralin	(140)
Ni Al	200	100 atm.	Tetralin	(252)
Ni–kieselguhr	200	100 kg.	Tetralin	(319)
Raney Ni	150	150 kg.	Tetralin	(237)
Raney Ni	170–200	150 kg.	Decalin	(237)
Raney Ni	100		Tetralin and decalin	(223)
Ni	180	Atmospheric	Tetralin	(255)
Ni	200	Atmospheric	Decalin	(255)
Cu–Cr	200		Tetralin	(223)
MoS₃	380	100 atm.	Tetralin	(246)
MoS₃	400	200 atm.	Tetralin and decalin	(245)
Na, NaH	270	120 kg.	Tetralin	(131, 33a)
Ca	270	2000 lb.	Tetralin	(33a)

270–300°C., at cold hydrogen pressures of about 120 kg. per square centimeter, and in the case of naphthalene catalyze the formation of tetralin.

The naphthols are more easily hydrogenated than naphthalene; with α-naphthol either ring may be hydrogenated preferentially, as Raney nickel at 150°C. causes hydrogenation to occur chiefly in the unsubstituted ring, and with copper chromite it is the substituted ring that is attacked (4). With β-naphthol,

α-Naphthol
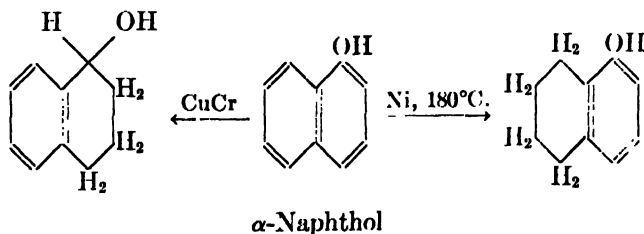
however, both catalysts cause hydrogenation to occur chiefly in the substituted ring (4, 50).

The hydrogenation of alkyl derivatives of naphthalene has not received much attention. Acenaphthene, like naphthalene, is hydrogenated to the tetrahydro stage in the presence of nickel at 210°C. and moderate pressures (47, 121); if the Sabatier-Senderens technique is used, at 150°C. a mixture of tetrahydro- and decahydro-acenaphthenes is obtained (121). α-Ethylnaphthalene can also be hydrogenated to the tetrahydro or decahydro stage over nickel (193).

3. Hydrogenation of anthracene

Anthracene can be hydrogenated in stages, the reaction usually proceeding to the octahydro stage, but the exact course of the hydrogenation is not clear. Schroeter (273) considered that the dihydro compound is an intermediate when nickel is used as a catalyst at 150-180°C. and 20 atm., and that this, in the presence of the catalyst, rearranges and is then hydrogenated further:
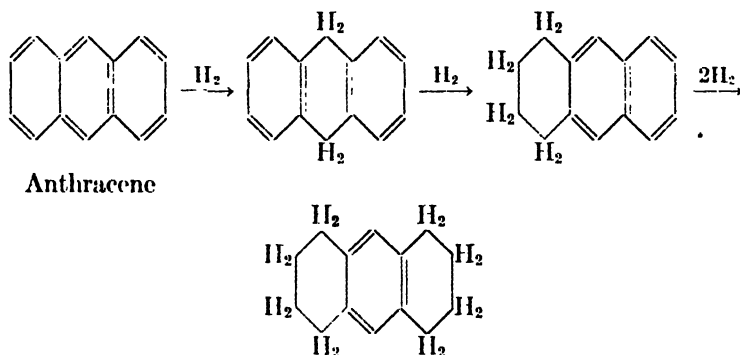
Anthracene

This mechanism is supported by the fact that the 9,10-tetraalkyldihydroanthracenes (I), in which a rearrangement such as that postulated above is not possible, are not hydrogenated in the presence of platinum black or Raney nickel at 200°C. and a pressure of 100 kg. per square centimeter, whereas the 9,10-dialkyldihydroanthracenes (II), which could rearrange, are hydrogenated under these conditions (208).

I   II
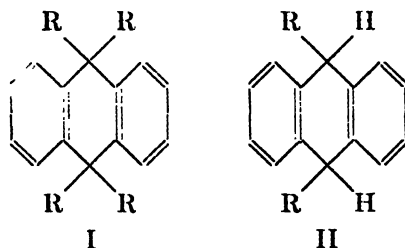
Fries, Schilling, and Littmann (110), on the other hand, do not consider that the 9,10-dihydro compound is necessarily an intermediate when platinum or nickel is the catalyst, for when 1 mole of hydrogen is added to 1 mole of

anthracene, only one-half of the theoretical amount of dihydro derivative is formed.   They suggested that two simultaneous processes occur, as follows:
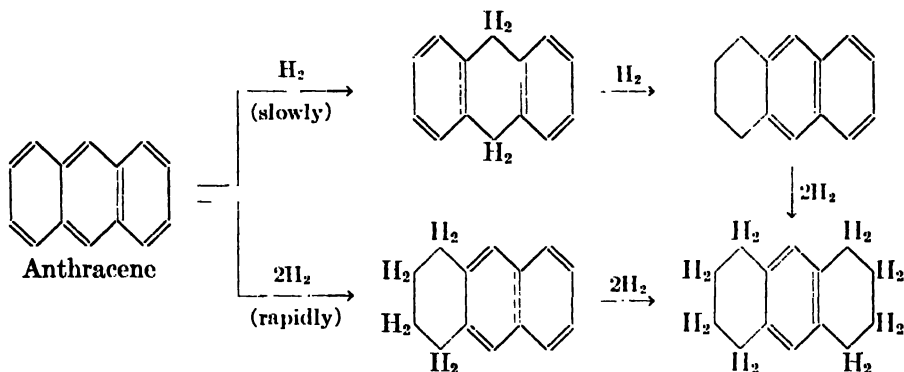
Fieser and Hershberg (103) have found evidence for the direct formation of the tetrahydro compound, not involving a meso dihydro as intermediate, from a study of the hydrogenation of benzanthracene and methylbenzanthracene. When either of these compounds (III) is hydrogenated in the presence of platinum black, it forms a tetrahydro derivative (IV).   Treatment of the original compound (III) with sodium, followed by hydrolysis, yields the meso dihydrobenzanthracene (V), and this on catalytic hydrogenation does *not* give the tetrahydro compound (IV), but rather a hexahydro derivative (VI), in which hydrogenation has occurred in another part of the ring system.
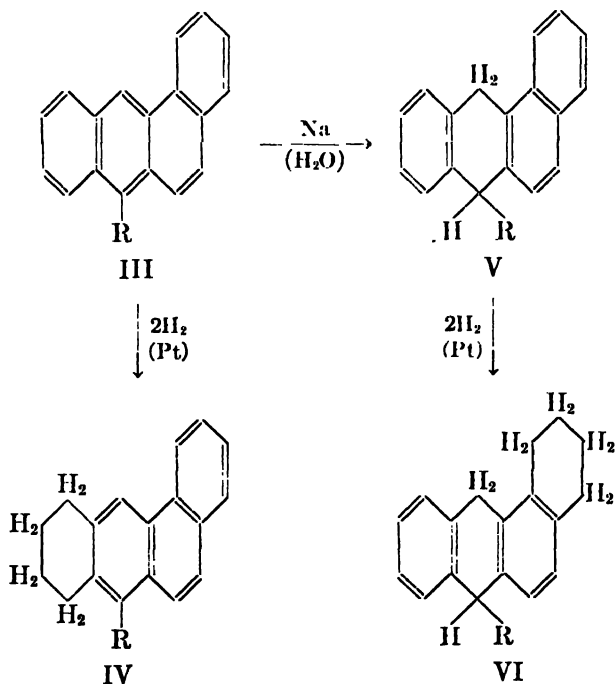
Anthracene can be converted to tetrahydroanthracene and a mixture of the octahydro compounds, in which the symmetrical form predominates, with a wide variety of catalysts, such as nickel–pumice at 160°C. (205), nickel–kieselguhr at 180 -280°C. (320), and molybdenum sulfide at 350°C. (247, 248). Both symmetrical and unsymmetrical octahydroanthracenes can be obtained; these have been shown to rearrange into each other under the conditions used. Long-continued hydrogenation of anthracene or of the octahydroanthracenes yields the perhydro derivative; this exists in at least two forms (110, 247, 248, 320).

4. Hydrogenation of phenanthrene

Like anthracene, phenanthrene can be hydrogenated stepwise, the first attack being at the 9,10-positions. The aliphatic nature of this double bond is demonstrated by the fact that it can be hydrogenated using copper chromite as catalyst, although this catalyst is generally inert for the hydrogenation of aromatic nuclei (79, 80).

Schroeter (274) has shown that the hydrogenation of phenanthrene occurs as indicated below, the steps being established by synthesis of the intermediates:
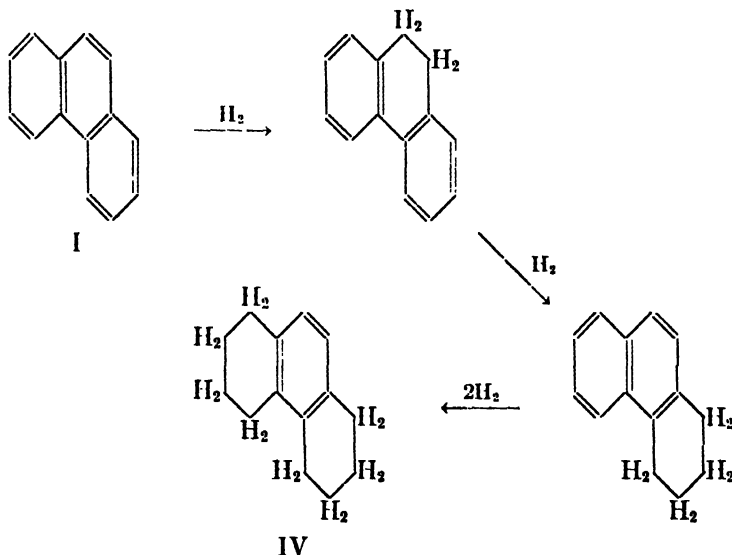
The reaction tends to stop at the octahydro stage; usually the symmetrical octahydro compound (IV) is obtained, but some of the unsymmetrical derivative (V) can be isolated when Raney nickel is used at 130°C. (80). The dodecahydrophenanthrene (VI) can be obtained if Raney nickel is used at 200°C. (80).

By a suitable choice of catalyst and conditions the lower hydrogenation products can be made to predominate; thus with a copper chromite catalyst at 150°C. the 9,10-dihydro compound is obtained (53); when Raney nickel is used at 110°C. (80), palladium black at room temperature (49), spongy palladium at

V   VI
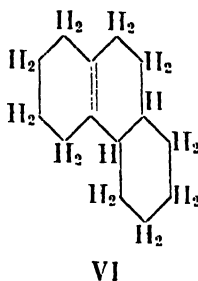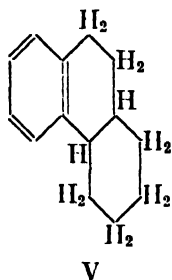
160°C. (49), or nickel at 150°C. (274), tetrahydrophenanthrene is formed. Strenuous hydrogenation causes the formation of a perhydro compound (4, 139, 247).

5. Hydrogenation of fluorene and indene

As would be expected, the isolated double bond of indene is readily hydrogenated (47, 220). Fluorene, on the other hand, is hard to hydrogenate, and with nickel oxide requires a long reaction time at 300°C. to form decahydrofluorene (262). With an osmium catalyst at 300°C. the main product is likewise the decahydro compound, but if a small amount of cerium oxide is present, the perhydrogenated product is formed almost entirely (262).

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THE PHOTOVOLTAIC EFFECT

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CONTENTS

I. INTRODUCTION

The photovoltaic effect is defined (VIII-2) as the production or change of potential between two electrodes separated by a suitable electrolyte or other substance when the electrodes are unsymmetrically illuminated. It is also called the "Becquerel effect" in honor of its discoverer, Becquerel. Similar to this effect is the "Swensson–Becquerel effect," which is the production of a photopotential upon illumination of the electrolyte only. In this paper we shall identify both the Becquerel effect and the Swensson–Becquerel effect as the photovoltaic effect. We shall limit our investigation to the "wet" type of cell, in which the electrodes are separated by a liquid.

It is the purpose of this paper to review the results of the research published about this phenomenon and to present the theories proposed to account for the mechanism producing it.

II. HISTORICAL

In 1839 Becquerel (IV-31) observed that an electric current was produced when he illuminated one of two similar platinum, gold, brass, or silver–silver halide electrodes immersed in dilute acid. This experiment closely followed his

observation (IV-30) that an electric current was produced on the illumination of a system consisting of a platinum electrode in each of two stratified liquids containing two substances which reacted with each other under the influence of light; this is regarded by Lange (VIII-4) as the birth-date of the photo-elements. Becquerel's discovery was followed by numerous investigations of workers with different types of "wet" cells and "dry" cells. Notably among these workers were Herz (VI-10) and Hallwachs (VI-9). The latter's discovery, in 1888, of the external photoeffect for the "dry"-type cell led to the develop-ment of the alkali photocells. The success in perfecting these cells and the interpretation of their mechanism diverted the attention of investigators from an intensive study of the "wet" type of cell originally used by Becquerel. How-ever, since that time a number of different types of "wet" cells have been in-vestigated and several theories have been proposed to interpret their mecha-nism. To date each theory seems to fit the experimental evidence for some cells but appears to be untenable as a general explanation for all types. A correlation of the available data seems to be necessary in an attempt to under-stand the mechanism involved in this process.

III. CLASSIFICATION OF PHOTOCELLS

Photocells may be classified in the following three main groups:

Group 1: Those dependent upon the alteration of conductivity by light. The selenium cells represent this group.

Group 2: Those dependent upon an *external* photoeffect, i.e., an electron emission from the outer surface under the influence of radiation and an ex-ternally applied potential. The alkali photocells represent this group.

Group 3: Those that we shall tentatively classify as dependent upon a so-called *internal* photoeffect. In this group Lange (VIII-4) places those cells showing the Becquerel effect, the crystal photoeffect, and the barrier-layer photoeffect. He presents evidence to show that the same fundamental process underlies all three of these types.

Several general characteristics that have been used to distinguish between the cells of Group 2 (photoelectric) and those of Group 3 (particularly the Becquerel type) are the following: (*1*) The photoelectric current is directly proportional to the light intensity; the photovoltaic potential is directly pro-portional to light intensity at low intensities and then to the logarithm of the intensity and finally reaches a steady maximum on increasing the light in-tensity. (*2*) No external potential is required for the photovoltaic cells. (*3*) The photovoltaic cells show reversals of polarity, whereas the photoelectric cells do not.

IV. CLASSIFICATION OF PHOTOVOLTAIC CELLS

The different kinds of photocells of Group 3 are of six general types:

Type I.   Metal electrodes immersed in solutions of electrolytes.

Type II.   Metal electrodes immersed in fluorescent solutions.

Type III.   Metal electrodes immersed in organic (non-fluorescent) liquids.

Type IV. Metal electrodes coated with inorganic compounds and immersed in solutions of electrolytes.

Type V. Metal electrodes coated with a dye and immersed in solutions of electrolytes.

Type VI. Metal electrodes separated by solid semiconductors. The first five of these types are the so-called "wet" type of cell and are discussed in this paper.

V. PHOTOVOLTAIC CELLS OF TYPE I: METAL ELECTRODES IMMERSED IN SOLUTIONS OF ELECTROLYTES

Cells of this type usually produce a relatively low photopotential unless the electrolyte is light sensitive, and even then considerable time may be required to reach the full value of the photopotential.

Becquerel (IV-31), in 1839, illuminated in turn one of two platinum, gold, or brass electrodes in a dilute acid with light of various colors and noted that (1) the current produced was greatest for light at the blue-violet end of the spectrum, (2) this current was not a thermoelectric effect, and (3) the illuminated electrode became positive with respect to the dark one. In 1859 Becquerel (IV-38) reported the following observations: (1) irradiated platinum, silver, and brass electrodes immersed in an electrolyte produced a current the direction of which depended on whether the electrolyte was acidic or alkaline; (2) the blue and violet parts of the spectrum were effective but not the red; (3) the effect was decreased if the platinum electrodes were heated and dipped in nitric acid; (4) the rays may have modified the state of equilibrium of the particles of the surface of the metal; and (5) polarization greatly increased the effect.

Grove (I-17), in 1858, reported that irradiated platinum plates in dilute sulfuric, hydrochloric, or nitric acid were sometimes positive and sometimes negative. He attributed the effect to an increase in the already existing polarization of the electrodes.

Pacinotti (I-23) illuminated copper plates in solutions of copper nitrate or copper sulfate, zinc in zinc sulfate or zinc chloride, iron in ferrous sulfate or ferrous chloride, lead in lead acetate, and silver in silver nitrate. In each case except silver, the illuminated electrode was negative. No effect was detected for platinum in copper sulfate.

Hankel (I-19) reported the following observations: illuminated copper in water became negative; copper in a slightly acid solution of copper sulfate first was negative but then became strongly positive; illuminated silver in water became negative; platinum became positive; silverized platinum became slightly positive; platinized silver became very strongly positive; and tin in water became negative. In all cases the effect was greatest in the blue region and least in the red. The sign of the thermal potential of copper in water was shown to be in the opposite direction from the potential upon irradiation.

Bose and Kochan (I-12), studying a cell with gold electrodes in sulfuric

acid, found that after polarization for 17 days the anode potential was lowered by violet light, unaffected by sodium light, and raised by red light. The potential varied to the extent of 0.1 volt, according to the nature of the light.

Buisson (I-13) found that the potential between a metal and an electrolyte was changed when the metal was plunged into the liquid after having been subjected to ultraviolet rays.

Wildermann (I-29, 30, 31, 32) found that for pure, carefully polished, illuminated silver or copper electrodes the potential was usually less than 1×10^{-4} volts. Upon irradiation the potential slowly increased to a constant value and decreased slowly to the original value when the light was withdrawn, the two periods being designated as "induction" and "deduction" periods. With irreversible cells, such as silver in potassium chloride, the photopotential changed in a complicated manner because of the action of opposing forces due to light and polarization. The potential which was calculated from the current flowing through a high resistance was directly proportional to the intensity of light and was a function of its composition. The photopotential of reversible cells, e.g., silver in silver nitrate, after the induction period, was proportional to the light intensity and independent of the salt solution. According to Wildermann (I-29), "Each kind of equilibrium between two states of matter becomes, at a constant volume on exposure to light, shifted in the direction which is accompanied by the greater absorption of light." .... "The law of mass action must hold good for equilibrium in homogeneous systems, when the equilibrium is shifted under the action of light to a new point in the same manner as in the dark." He concluded that the photopotential was due solely to a change in solution pressure of the electrode, on the basis that an equilibrium could be established for light as it had been set up for heat by van't Hoff.

Athanasiu (I-1) studied cells made of silver, copper, nickel, zinc, and cadmium electrodes immersed in $0.25 N$ solutions of their salts. He (I-2, 3) attributed the effect to an alteration of the electrode surface (which became visibly tarnished) and to a heat effect upon irradiation, the two effects being superimposed. Copeland (I-16), Black (I-11), and Clark (I-14, 15) investigated the thermal potential of silver electrodes and concluded that the potentials developed on illumination of silver electrodes were not the direct result of temperature effects, because long wave lengths of light were relatively ineffective in developing photopotentials, and the thermal potential developed was very often of the opposite sign to that of the photopotential.

Schliviteh (I-26) reported photopotentials of 0.7–12 millivolts when using platinum electrodes in solutions of sodium nitrate, potassium dichromate, and ammonium dichromate. When the illumination ceased, the potential changed from its negative value to zero, and for concentrated solutions to a positive value.

Sihvonen (I-27) studied cells of pure metals (e.g., platinum, silver, copper, nickel, iron, chromium, zinc, aluminum, and mercury) in solutions of inorganic

acids, bases, and salts. He considered the photoeffect to be the resultant of (1) photoelectric effects at the electrode, (2) adsorbed films of gas on the electrode, and (3) ions in solution. He accounted for the results on the basis of five possible reactions: namely, (1) liberation from the metal of an electron which solvates in solution; (2) discharge of cations by electrons when the electrode is illuminated with current flowing; (3) formation of anions from the adsorbed gas on the electrode; (4) photovoltaic discharge of anions; and (5) photovoltaic formation of cations from adsorbed gas on the electrode.

Audubert (I-5, 6) reported that platinum, copper, and mercury functioned as anodes (emitted electrons to the solution) upon illumination, while silver and gold functioned as cathodes irrespective of the electrolyte. Potentials of 10^{-7} to 10^{-5} volts were developed. From these studies he drew the following conclusions: (1) That the potentials were not due to a layer of impurity, as proposed by Berthelot (IV-40). (2) That light of short wave length was more effective than that of long wave length. The threshold frequency seemed displaced toward the short wave length the higher the solution pressure of the electrode, and the sensitivities varied inversely with the solution pressure. (3) That the influence of the cation was small and that of the anion was apparently zero. (4) That positive polarization diminished the photovoltaic effect of metals acting as anodes when illuminated but negative polarization increased it, while the opposite was true for cathodes. At high polarizations the sign of the effect was reversed. This suggests a mechanism for the photovoltaic effect which closely resembles that of the photoelectric effect.

Audubert (I-8) also studied gold and platinum electrodes in solutions of various pH values and concluded that the inversion was independent of the frequency of the radiation and independent of the concentration of the electrolyte but depended mainly on the potential of the metal and also on the acidity, basicity, or neutral nature of the electrolyte. Further work (I-9, 10) with gold and platinum electrodes, using different colored light, led him to suggest that the photopotential was due to photolysis of water. The molecules of water were assumed to become fixed to the electrode, to absorb radiations not usually absorbed, and to liberate oxygen and hydrogen, which depolarized the electrodes.

The threshold values of metal electrodes were investigated by Copeland (I-16) (for silver electrodes) and by Clark (I-14, 15) (for copper, silver, and gold electrodes) immersed in solutions of potassium chloride, potassium bromide, potassium nitrate, etc. They found that light of wave length longer than 4900 Å. was ineffective in producing a photopotential; a slight effect was noted at 5500 Å., but Clark and Garrett (I-15) attributed that to a coating on the electrode. Figure 1 shows a typical curve for the wave length vs. photopotential for such pure metals. This threshold value is compared with those obtained for the same metals in a vacuum but at various stages of outgassing; that comparison is shown in table 1. Columns 3, 4, and 5 were compiled from those given by Hughes and DuBridge (VIII-2, page 75).

Clark (I-14) observed that most of the cells studied gave a positive photo-potential (illuminated electrode the anode). Some of the cells he studied gave a negative photopotential, but all of them gave the same threshold value regardless of the sign of the photopotential. The solutions used for the determination of these threshold values do not absorb in the region of this photo-
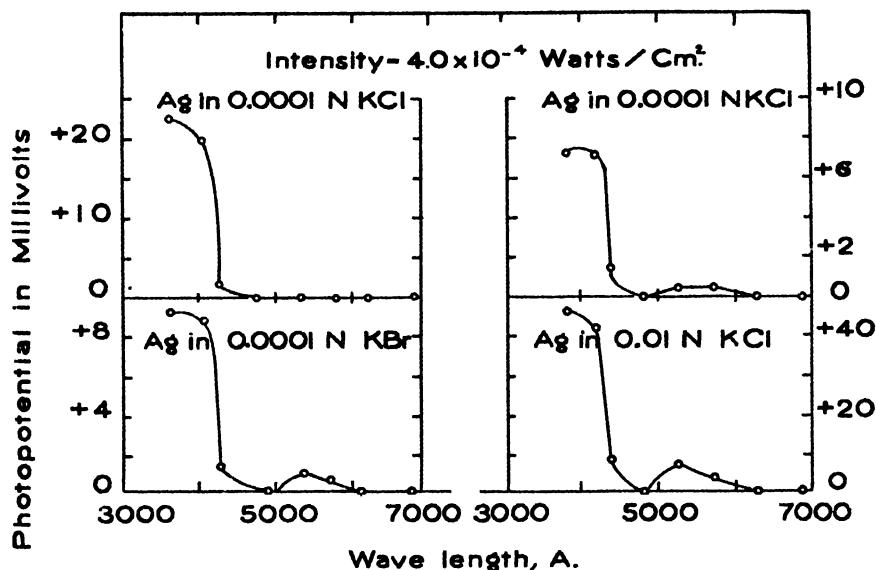
Fig. 1. Typical curve for the wave length vs. photopotential for pure metals

TABLE 1

Approximate photoelectric thresholds of silver, gold, and copper

METAL	METAL IN SOLUTION	THRESHOLD WAVE LENGTH; METAL IN A VACUUM		
		No outgassing	Partial outgassing	Extended outgassing
		A.	A.	A.
Silver.....................	4900	3200–3400	2900–3100	2600–2700
Gold.......................	4900	2625	2600–2800	2650–2610
Copper....................	4900	2700–3000	2700–3000	

activity. The inference from this work is that the effect in the cells studied by Copeland and Clark is photoelectric in origin.

Copeland and Clark detected a change in sign of the photopotential with concentration of the electrolyte. This was investigated by Black (I-11), who reported that cells containing silver electrodes in electrolytes of low concentration (below 0.05 molar for most salts studied) in general gave positive photopotentials but at high concentrations (above 0.2 molar) gave negative photopotentials (the illuminated electrode became more negative, and then the dark electrode). His results are summarized in table 2. This observation

throws some doubt on the conclusions of Audubert (I-5, 6) and of Schlivitch (I-26), who reported that the illuminated electrodes were positive in solutions

TABLE 2

Sign of photopotential for silver electrodes in several electrolytes

ELECTROLYTE	NORMALITY	SIGN OF PHOTOPOTENTIAL (EACH SIGN IS THAT OF A DIFFERENT CELL)
KCl	0.20	−+
	0.18	−−
	0.16	−−
	0.14	−−−
	0.12	++
	0.10	+
KBr	0.15	−−−
	0.12	−−−−
	0.10	−−+
	0.06	−−+−−−
	0.04	−−−−+
	0.02	++++
KI	0.20	−−−
	0.18	−−
	0.16	−−
	0.14	++++
	0.12	++
	0.10	++
KCN	0.50	−−
	0.30	−−
	0.10	−−
	0.07	+−−−
	0.04	++
	0.01	+
KNO₃	0.50	−−−
	0.35	−−
	0.20	++
	0.10	++
	0.05	++
	0.02	++
K₂CrO₄	0.10	−
	0.07	−
	0.06	−
	0.05	−
	0.04	++
	0.03	++

of some salts and negative in others, for the effect may have been due to the magnitude of the concentrations used; however, the effect of pH change on the sign of the potential should be determined for these solutions.

Studies have been reported of several cells containing metal electrodes in electrolytes which are known to be light sensitive. Baur (II-1) reported a small positive effect on illuminating platinum electrodes in solutions containing ferrous and ferric chlorides, mercurous and mercuric chlorides, and cerous–ceric salts. Iimori (I-20) studied cells composed of platinum electrodes in potassium ferrocyanide and obtained a negative potential. This he attributed to the reaction

$$Fe(CN)_6^{-4} + 2H_2O \xrightarrow{\text{light}} Fe(CN)_5H_2O^{-3} + OH^- + HCN$$
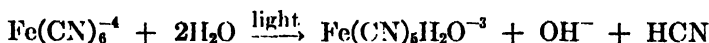
The photochemical effect was greatest at 4400–4500 Å. He reported a positive potential for platinum electrodes in solutions of potassium nickel cyanide and potassium platinum cyanide (I-21). This he attributed to a type of complex-ion formation rather than to a photoelectric effect. Audubert (I-7) studied cells with platinum electrodes immersed in solutions of $Fe^{+++} \mid Fe^{++}$ and of $I^- \mid I_2$. In the case of the $Fe^{+++} \mid Fe^{++}$ solution the reaction

$$Fe^{+++} \xrightarrow{\text{light}} Fe^{++}$$
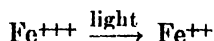
was used to account for the observed potential; in the $I^- \mid I_2$ solutions, the addition of iodine changed the potential from negative to positive, owing to the formation of the trihalide ion. He interpreted his data quantitatively in terms of these equilibria.

Sasaki and Nakamura (I-24) reported a photopotential for the reversible reaction:

$$Fe^{+++} + I^- \underset{\text{light}}{\overset{\text{dark}}{\rightleftarrows}} Fe^{++} + I$$
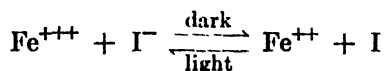
which proceeded in the dark and reversed in the light. The change of potential with iodine concentration was identical in the light with that in darkness.

Schiller (I-25) studied the Becquerel effect of molar solutions of potassium oxalate containing varying amounts of ferrous and ferric salts. Pure ferrous salt showed a change of potential, but the potential rose faster the greater the proportion of ferric salt present. He accepted Baur's theory as fitting all the facts better than the theory of photoelectric emission.

Swensson (I-28) worked with platinum electrodes in solutions of cupric sulfate, nickelous sulfate, zinc sulfate, and sulfuric acid. He rejected Baur's (II-1) photolysis theory, because there was no formation of hydrogen, oxygen, hydrogen peroxide, or ozone, and suggested that the electrodes probably became polarized. He found an initial negative effect which changed to positive on continued illumination. He observed that a potential was produced when the electrolyte only was illuminated, and he concluded that the phenomenon did not depend on the illumination of the electrode but was due entirely to the effect of light on the solution. He assumed that light reversibly changed the molecules from form A to form B at a rate proportional to the concentra-

tion of A and the light intensity. Thus an absorption of light resulted in a change in energy content, producing a corresponding change of potential.

Mukhin and Zilberfarb (I-22) studied the influence of radiation on the electrolyte only in a cell containing a platinum electrode in sulfuric acid at various concentrations. They measured both the thermal potential (negative at all concentrations) and the photopotential. The effects due solely to the light were as follows: negative potential at 0.05 M, maximum positive potential at 0.49 M, and negative potential again at 1.24 M, because of the two opposing processes occurring in the electrolyte.

Adler (VI-1) has extended Kimball's (VI-11) theory of the absolute reaction rates at electrodes to the positive primary photopotential and has shown that the derived formula reduces to the equation

$$\text{Potential} = \text{Constant} + kI$$

where I is the intensity of illumination, for pure metal electrodes of very low intensities and to

$$\text{Potential} = \text{Constant} + k' \ln I$$

for active electrodes such as the oxide, sulfide, or halides of copper or silver. Both of these equations are in agreement with experimental data.

Gibney and Dole (VII-16) studied the cell

$$\text{Na} \mid \text{NaI in } C_5H_{11}NH_2 \mid \text{Na}$$
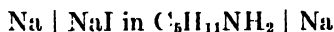
using a 200-watt tungsten lamp and a mercury-vapor arc and found no photovoltaic effect for sodium in the absence of water. The energy supplied to the electrons by visible light was not sufficient to cause the transition of the electron from metal to solution. Gibney and Dole suggested that the presence of sodium ions in solution may modify the energy relation of the electrons, and that the stable energy level of electrons in monoamylamine may be so high that the electrons in metal illuminated by visible light cannot make the transition from metal to solution.

Summary on photovoltaic cells of Type I

These data would suggest that the photochemical theory is probably applicable to those cells containing an electrolyte that is light sensitive. For other cells the primary effect seems to be either the photoelectric effect, the photolysis effect, or a combination of both, while the thermal effect is secondary and slight. It seems highly probable that the observed photopotential may be the resultant of more than a single mechanism.

VI. PHOTOVOLTAIC CELLS OF TYPE II: METAL ELECTRODES IMMERSED IN FLUORESCENT SOLUTIONS

Early work with these solutions was concerned with the effect of light on their electrical conductivity (II-5, 6, 36; VII-25).

Nichols and Merritt (II-33), in studies with eosin, fluorescein, rhodamine, naphthalene-roth, and cyanin dissolved in absolute alcohol found an increase in electrical conductivity which reached its full value at once. As soon as the light was cut off, the conductivity returned to its dark value. The relation of this effect to fluorescence was indicated by the observation that only those rays which excited fluorescence changed the conductivity, and that the light that caused the most intense fluorescence produced the greatest change in conductivity.

Goldmann (II-7), in 1908, studied platinum electrodes pressed flat against the inside wall of the illuminated side of the cell and transparent platinum mirrors on glass. He reported that the changes of conductivity of fluorescent solutions were caused by the absorption of light in the solution layer in close proximity to the electrode. The current was proportional to the amount of electrode surface illuminated and to the light intensity. Goldmann concluded that the effect depended upon absorption but not on fluorescence, since solutions which did not fluoresce gave effects of the same magnitude as those which did.

Hodge (II-19) found that if the electrodes were entirely concealed from light, or if the liquid was moved rapidly past the electrode, no change of conductivity as great as 0.1 per cent was produced when the liquid was illuminated. In all cases when alcoholic solutions of fluorescent electrolytes were used, the exposed electrode became positive with respect to the unexposed one, although aqueous fluorescein produced a potential of opposite sign.

Hodge (II-20) reported an increase of 10 to 15 per cent in the conductivity of an alcoholic solution of eosin on exposure to light. He drew the following conclusions: (1) The effect is not thermal, for the temperature coefficient is not more than 1 to 5 per cent per degree, the light effect is about the same with the cell in ice water, and there is a quicker light and dark response than that due to heat. (2) There is no change in the conductivity of the liquid unless a region very near the electrodes is illuminated. (3) An immediate decrease of resistance followed by an increase, which is reversed on removing illumination, suggests a combination of two effects, one growing to a maximum more rapidly than the other and decreasing more slowly. (4) The maximum potentials with the application of no external E.M.F. are obtained at the infrared edge of the absorption band for eosin, fluorescein, naphthalene-roth, and rhodamine, the last dye showing a potential of 0.2 volt.

Rassenfosse (VII-22) noted that the electrical conductivity of eosin and fluorescein was greatest when illuminated by light of a wave length most absorbed by the solution, but Pienkowski (VII-20) observed no change in conductivity when these same materials in water, alcohol, or gelatin were illuminated by white or monochromatic light, under conditions preventing heating and polarization. Von Samsonow (VIII-10), in experiments with uranyl and quinine sulfates and with chlorophyll, found the maximum effect in the spectrum region of greatest absorption.

Baur (II-1), in 1908, reported a negative effect upon illuminating platinum electrodes in a solution containing both uranous and uranyl salts. Titlestad (VIII-14) confirmed this observation, using varied relative concentrations of uranous and uranyl sulfates acidified with sulfuric acid. The greatest effect was in the blue and violet range of 4230–4840 Å. The rate of increase of potential plotted against the potential was linear for the ascending curve, but the rate of decrease was proportional to the square of the potential and the maximum potential was proportional to the logarithm of the intensity of the light. The study of dilution, varied concentration of sulfuric acid, and addition of alcohol indicated that the mass-action law of Wildermann (I-29, 30, 31, 32) was not obeyed. Baur (VII-5), commenting on Titlestad's paper, suggested that absorption of light made uranous salts more negative and uranyl salts more positive, and that the former effect usually predominates. He derived mathematical expressions for the ascending curve during illumination and for the descending curve after extinction. He ascribed this effect to a change in thermodynamic potential resulting from the absorption of light and the subsequent induced reaction. If the absorption is high and the reaction slow, the change in potential is proportional to the logarithm of the intensity of the light, whereas if absorption is low and reaction velocity is high, the change in potential is directly proportional to the light intensity. Baur (II-2) postulated that light changed uranium ions to the octavalent and quadrivalent states; in the dark the two reunite to yield the hexavalent form, giving off absorbed light in the form of fluorescence. He found that chloride or iodide ions, ferric and vanadyl salts, vanadic acid, and quadrivalent uranium salts extinguished the fluorescence and also destroyed the Becquerel effect. In 1921 Baur (II-3) found that the photocurrent was increased by the illumination of polarized platinum electrodes in solutions of uranyl sulfate, eosin, and quinine sulfate; he suggested that the depolarization of light might have its origin in the photolysis of water. Baur and Rebmann (II-4) concluded that continuous photolysis of water can occur only if the system excludes the recombination of hydrogen and oxygen.

Trümpler (VII-27) studied the illumination of the urano-uranyl sulfate system and found that a positive or negative effect may result in the presence of small quantities of other substances. The negative effect was diminished by iodine, hydrogen iodide, hydrogen chloride, vanadium sulfate, ferrous sulfate, and ferric sulfate, and in some cases the effect appeared to be changed from negative to positive. The positive effect was diminished by sulfur dioxide, uranic sulfate, and oxalic acid. The substances which exerted either a positive or a negative influence on the Becquerel effect also decreased the fluorescence of uranyl sulfate solutions. The cause of the Becquerel effect in these cells was considered to be the result of raising the uranyl ions to a higher valence state. Hatt (II-18) studied uranyl formate and found that the uranous salt (one of the products of the light reaction) retarded photolysis (II-3). Potassium iodide, potassium chloride, ferric chloride, vanadyl sulfate, and vanadic acid also retarded the reaction.

Thompson (II-42) used thin films of metals fastened to the front wall of the cell to eliminate absorption by the fluorescein, fuchsin, etc., between the light source and the electrode. He carefully made correction for unequal dispersion and energy distribution throughout the spectrum. His results may be summarized as follows: (1) Curves for the growth and decay of the "photoelectric current" are similar to those for fluorescence. (2) There is no close connection between the photoelectric current and fluorescence, for two methods of increasing the fluorescence do not increase the current. The region for excitation extends farther into the red than for fluorescence. (3) The magnitude of the photoelectric current depends on the metal. Only platinum, silver, gold, and oxidized copper, of the ten metals tested, gave a measurable effect. (4) The effect is not the photoelectric effect of the metal in the liquid, for the position of the maximum depends on the material in solution, not on the electrode. (5) All curves show a maximum photoelectric current approximately in the region of maximum absorption of the solution.

Stacchelin (II-41), after an extensive study of the photovoltaic effect of platinum in fluorescent dyes in the absence and presence of oxidizing agents, concluded that the effect is bilateral, its magnitude and direction depending on the reducing or oxidizing agent present, and that the behavior can be explained on the assumption of a "latent knall-gas" photolysis.

Jenkins (II-21), using identical semitransparent films of platinum sputtered on the glass walls of a cell containing alcoholic solutions of rhodamine B made the following observations: (1) The sensitiveness of the current increases to a maximum for 3 per cent concentration and then decreases. (This is contrary to Goldmann's observation (II-7) of a continuous increase with concentration.) (2) There is an apparent increase of sensitiveness, which may be due to the failure of the molecules changed by light to return to their original condition. (3) A stream of electrolyte flowing against an electrode causes it to become more negative, temporarily, irrespective of its previous charge. The magnitude of the negative potential is a function of the force with which the liquid strikes the electrode.

Grumbach (II-10) studied cells made of platinum electrodes immersed in solutions of fluorescent substances previously illuminated by a mercury arc and obtained an effect showing that the potential was due at least in part to the modification of the electrolyte with light. A reversal from a negative to a positive potential was noted with 0.05 per cent uranin. Grumbach suggested that the electrodes adsorb the photoproduct, forming a true concentration cell. He (II-11) further confirmed his theory of a potential due to the adsorption of light-modified molecules on the electrode surface plus a Becquerel effect of the fluorescent solution by the following observation: Illumination of a platinum electrode in sodium fluoresceinate produced a positive potential, while illumination of the liquid about 15 mm. from the electrode produced a negative potential. Using the potassium salt of sulfofluorene, Grumbach (II-12, 13) confirmed his generalization as to the rôle of adsorption and indicated the necessity of intro-

ducing the concept of electrolytic dissociation into the theory of the electromotive force of adsorption. According to him (II-14), each measured photopotential in fluorescent electrolytes is the algebraic sum of the potential of adsorption and the Becquerel effect. Grumbach (I-18) further showed these two effects by the illumination of platinum electrodes in glycerol solutions and in glycerol–sodium fluoresceinate mixtures.

Platinum electrodes in sodium fluoresceinate exposed to oxygen of the air produced a potential of 5 millivolts on illumination but no potential in a vacuum (II-15). In a cell containing sodium fluoresceinate in 40 per cent glycerol, the Becquerel effect in air was negative but much more negative in a vacuum.

Schlivitch (II-40) confirmed Grumbach's observation of the effect of air by the observation that the potential of a photovoltaic cell consisting of platinum electrodes in aqueous uranin depended on the amount of dissolved oxygen.

Grumbach and Taboury (II-16, 17) reported that the potential of the photo-cell

$$Pt \mid fluorescein\text{--}sulfuric\ acid \mid Pt$$
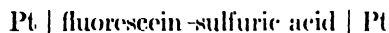
assumed discontinuous values given by the equation

$$E = nE_1$$

in which n is a whole number and $E_1 = 1.3 \times 10^{-3}$ volts. This, the "law of equidistances," was explained on the basis of the adsorption of successive monomolecular layers.

Murdock (II-30) suggested that the equations of Goldmann (II-7) and of Thompson (II-42) have no physical significance; he showed that these equations do not represent the experimental data even after corrections are made for damping and inertia of the galvanometer. This casts doubt on Goldmann's mechanism of a photoelectric action. Murdock (II-31) made use of a device similar to Goldmann's cell, whereby the electrolyte could be illuminated before, during, and after flowing by the electrode. He also agreed with Grumbach (II-10, 11, 12, 13) that the effect was due largely to a change of the electrolyte by the light, even when the electrode was not illuminated. He thought it probable, but not certain, that illumination of the electrode resulted in an E.M.F., with polarization playing an important rôle. Later (II-32) he considered that the apparent constancy of current with external resistance was probably due to the fact that the external resistance was small relative to the internal resistance of the cell.

Rule (II-38) illuminated electrodes through the electrolyte (alkaline fluorescein solution), and concluded that variations arose because of the formation of a concentration cell by means of the photochemical changes of the electrolyte. The same electrodes in alkaline solutions in the absence of fluorescein gave no photopotential. He noted a maximum effect (II-37) for a particular concentration of electrolyte (fluorescein), which he attributed to the parallel occurrence of fluorescence. When the molecule receives a quantum of radiation it passes

to a critical state from which it returns to its original stable state or another stable state by emitting fluorescent radiation. As the concentration increases, the number of activated molecules increases and the E.M.F. increases to a maximum where the "protective" effect of adjacent molecules removes a part of the energy, thus decreasing the E.M.F. During illumination he observed an initial small positive potential which changed to a negative potential and increased to a maximum value.

Russell (II-39) derived an equation for the variation of the potential with time, using the theory of photochemical modification and the effect of diffusion on the potential developed. He described in detail each step, arriving at the equation

$$E = K \log \left(T_i^{1/2} - t_i^{1/2} + \frac{t_i}{2T_i^{1/2}} - \frac{t_i^2}{8T_i^{1/2}} + \frac{B}{I} \right) - K \log \frac{B}{I}$$

where T_i = time during illumination,

t_i = time in the dark,

I = intensity of the light,

K = $\frac{RT}{nF} \ln 10$, and

B = constant.

To test his theory, Russell (II-39) used platinum electrodes (so thin as to be transparent), sputtered on glass in a 3 per cent solution of rhodamine B in absolute alcohol. He obtained a straight line by plotting photopotential *vs.* log $(T_i^{1/2} + B/I)$, as called for by the theory, except where the photopotential was small. This, he explained, was due to a small constant negative photopotential built up in the first few moments of illumination, as above noted by Wildermann (II-43), Grumbach (II-10, 12, 13), and Rule (II-38). This suggests the intermediate compound indicated by Wood (II-45). The results for decay were in better agreement with the theory than for growth, again indicating that during illumination there was present some source of photopotential not considered in the theory. A further test of the importance of diffusion was shown by the lag between the illumination and the change of potential. Russell (II-39) concluded that the material causing the photopotential is formed at or near the place where the light enters the dye and that diffusion is an important factor in controlling the potential–time relation. He found no evidence indicating the presence of the Hallwachs photoelectric effect.

Lifshitz and coworkers (II-22 to 27; VI-12) have studied the photovoltaic effect of platinum in solutions of dyes. They have drawn a number of conclusions from their own work and from discussions of the work of others:

(*1*) The results of Swensson (I-28) have been confirmed (II-22).

(*2*) The photovoltaic effect in dyes is independent of the hydrogen-ion concentration (II-23).

(3) The effect is ascribed to the after-effects of a photochemical change in the electrolyte (II-22 to 25).

(4) Both positive and negative effects are observed, dependent upon the nature of the ions (II-23).

(5) The Becquerel effect is the electrochemical consequence of the primary photochemical process in which some electrons are thrown into another orbit by the action of light (VI-12).

(6) The magnitude of the effect is greatly influenced by impurities (II-23, 25).

(7) The Swensson–Becquerel effect is not present at reversible metal–metal ion electrodes or at hydrogen electrodes. It is shown only at polarizable electrodes or at phase boundaries (II-23).

(8) It is difficult to distinguish between surface effects at the light-sensitive electrodes (effects of the first kind) and volume effects in the electrolytic solution (effects of the second kind) which are suggested by Winther (II-44); the latter does not depend on a simple photochemical displacement (II-25).

(9) The effect occurs in non-aqueous solutions (II-25).

(10) The effect depends on the nature of the solvent, the kind of ions, the wave length and intensity of the light, and the temperature (II-25, 26).

(11) The effect is independent of (a) the external and internal cell resistance, (b) the nature of the non-polarizable electrode, (c) the duration of light exposure, (d) the polarization and electrode potentials, (e) the size and shape of the electrode, and (f) the volume of the exposed solution (II-29, 34).

Lowry (II-28, 29) reported the results of a very precise and extensive research on the location of the seat of the photopotential with platinum electrodes in fluorescent dye solutions. He used an apparatus patterned after that of Murdock (II-30, 31, 32), whereby the electrolyte was circulated concentrically about two narrow strips of platinum sputtered on the outside of a Pyrex test tube mounted on a vertical brass tube. For illumination, a small rectangular window was cut in the lower end of the brass tube. The electrode could be turned in front or on either side of the window through a range of more than 180°, so that the electrolyte could be illuminated before, during, or after contact with the electrode. The electrolyte about the test tubes was contained in a rotating bottle, and the whole was placed in a constant temperature bath.

Lowry (II-29) formulated the following conclusions: (1) The photovoltaic effect for rhodamine B is due entirely to the modification of the electrolyte with light. (2) The effect follows the laws of the concentration theory, the concentration of the modified form B varying with the light intensity, the time of illumination, and the concentration of material A. (3) There is no indication of any effect due to the direct illumination of the electrode-electrolyte boundary. This is indicated by the smooth curve rather than an abrupt change of slope in going from one region to another. (4) There is no reversal of photopotential for rhodamine B and uranin at the beginning or end of illumination, as noted above by Rule (II-38). However, values of the potential for short periods of illumination are reported which deviate from the theory.

Ghosh (VIII-15), in a study of polished platinum electrodes in alkaline solutions of fluorescein, postulated the reaction

$$B \rightleftharpoons B^+ + e$$
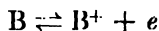
at an electrode and applied the Nernst equation to the reactions at the light and dark electrodes.   According to Ghosh, the excited molecule of the fluorescent substance gives with a second normal molecule an unstable intermediate B, which in turn can combine with a second molecule of B to form C.   The potential depends on the concentration of the intermediate B, the velocity of formation of which is proportional to the light intensity and the deactivation velocity of which is proportional to the square of the concentration.

Rao (VII-21) illuminated platinum-foil electrodes in aqueous solutions of erythrosin and chrysoidine and found that their photopotentials (negative for erythrosin and positive for chrysoidine) varied directly as the square root of the light intensity.   The wave lengths immediately following the long-wave-length limit of the absorption band of the dye were most effective.   After a review of various theories of the effect, it was concluded that the diffusion of activated molecules to the electrode seemed best to explain the potential curves for various concentrations.

Pincussen, Suzuki, and Seitz (II-34) obtained curves for extract of visual purple and for the solvent, both in the dark and in the light.   The reversible phenomena of the curves were attributed to the photovoltaic effect of the solvent.

Summary on photovoltaic cells of Type II

The conclusions of the workers in the field indicate that the principal effect for this type of cell is probably photochemical rather than photoelectric.   The thermal effect and the photoelectric effect may be present but, if so, they must be small.

VII. PHOTOVOLTAIC CELLS OF TYPE III: METAL ELECTRODES IMMERSED IN ORGANIC (NON-FLUORESCENT) LIQUIDS

Of the many possible cells of this type, those prepared from Grignard solutions have received considerable attention.   Historically, the photoeffect of such solutions was investigated as a result of the observation that luminescence is often associated with the reactions of Grignard reagents (III-6, 7, 8, 17, 21, 22, 23, 24).   Moreover, it was observed by Dufford and coworkers (III-8, 9, 10) that light was emitted at the anode when potentials up to 1500 volts were applied to luminescent solutions.   This observation suggested to them that the converse might be true: namely, that a potential difference might be produced upon the illumination of electrodes in Grignard reagents.   Dufford (III-3, 11) prepared cells containing Grignard reagents with platinum for the electrode to be illuminated and other metals for the dark electrode; the potentials were measured with a potentiometer.   His results were as follows: (1) Of the eight

metals tested (platinum, gold, magnesium, lead, zinc, copper, aluminum, iron), the combinations platinum–aluminum, platinum-copper, and platinum lead seem best. (2) Aromatic compounds give stronger responses than aliphatic. (3) The order of sensitivity is RMgCl > RMgBr > RMgI. (4) The optimum concentration seems to be 1 M for aromatic and 0.5 M for aliphatic Grignard solutions. (5) Some Grignard solutions show a reversal of the initial response on continued illumination. (6) The light sensitivity seems to spread throughout the entire visible spectrum, with a broad maximum in the green or blue. (7) The voltage change is not a thermal effect, for (a) the rate of change of voltage averages only about 0.002 volt per degree, (b) the direction of the thermal effect is the reverse of the light response, and (c) cells in ice water give about the same response as at 25°C.

With several refinements in his apparatus, i. e., fresh distillation of ether over sodium, use of sodium-free ether, preparation of the compounds in a nitrogen atmosphere, and use of an H-type of cell to make certain of illumination of only one electrode, Dufford (III-13, 16) reported the following results:

(1) For the initial response, the potential is proportional to the intensity. For the total response, the potential is proportional to the logarithm of the intensity.

(2) There is a slight photovoltaic effect with platinum–aluminum electrodes in pure ether.

(3) The first response is usually positive, but after two or three illuminations it becomes and remains negative.

(4) Depolarizers such as ethyl bromide, methyl iodide, and benzyl chloride greatly increase the current and the voltage.

(5) A positive response is obtained with magnesium, aluminum, copper, zinc, lead, and iron as the illuminated electrodes, but a negative response with platinum.

(6) The positive response is not due to occluded oxygen, for (a) there is no observable difference after outgassing platinum by heating in hydrogen at 80°C. for several hours and allowing it to cool in hydrogen, and (b) there is no observable difference after electrodes are kept between freshly cut surfaces of sodium for several days.

(7) An apparatus was devised for circulating the electrolyte past three electrodes, the middle one being illuminated and the "upstream" one maintained as a reference. With the solution at rest, illuminating the middle electrode did not affect the "downstream" electrode. The effect was the same when the middle electrode was removed and only the electrolyte illuminated. The solution clearly carried with it something that reduced the potential of the "downstream" electrode.

Recently it has been observed (III-14) that magnesium electrodes cleaned by reaction with organic halides are "inactive" but when exposed to oxygen they become light sensitive. A surface film appears to be necessary for light sensitivity in the case of magnesium electrodes.

Hammond (III-19) reports the following observations of Grignard photo-cells: (*1*) The photopotential is affected by agitation, polarization, cleaning, or brief exposure to air. (*2*) There are no noticeable temperature changes. (*3*) Oscillations of potential in the dark occur, owing to some unknown cause. (*4*) The potential changes with the age of the cell, owing to concentration changes and to slow electrolysis caused by leakage currents. (*5*) Illumination of the electrolyte alone gives very small effects, which are attributed to scattered light reaching the electrodes. Thus the seat of the phenomena is located at or near the surfaces of the electrodes, near enough to be affected by changes on the electrode surfaces. (*6*) Several types of cells give responses of 0.2 to 0.8 volt when exposed to x-rays (III-15, 19), which differ in magnitude and frequently in sign from the photovoltaic effect of the same cells with visible light. (*7*) It is impossible to trace any general interrelation between the changes in poten-tial, resistance, and capacitance or illumination. (*8*) The photoelectric hy-pothesis is untenable, for it seems unreasonable to attribute a voltage variation of 10 to 50 per cent to a process causing a resistance change of only 1 to 2 per cent.

Harty (III-20) studied the influence of depolarizers on the photovoltaic effect in Grignard solutions. He used copper, zinc, aluminum, iron, lead, and plat-inum electrodes in ethylmagnesium bromide and phenylmagnesium bromide with ethyl bromide and ethyl iodide as depolarizers. Special care was taken to keep the Grignard solutions dry. The cells contained about 40 cc. of Grignard solution and 1 cc. of depolarizer, that having been shown to be the best con-centration.

Harty drew the following conclusions: (*1*) The value of the dark voltage occurs as if it were a matter of chance, ranging from 0 to 40 millivolts, with no good reason discovered. (*2*) The data fail to reveal any uniformity in the effects due to polarizing the electrodes either anodically or cathodically. (*3*) The ca-pacitance of cells filled with ethylmagnesium bromide is greater than for phenyl-magnesium bromide, as expected if Hammond's (III-19) calculations, showing a monomolecular layer, are correct, because of the thinner layer of the former. (*4*) The direct current resistance (a function of the thickness) of phenylmag-nesium bromide should be greater than for ethylmagnesium bromide, as found by Hammond and Harty.

Dufford (III-16) concluded that the photovoltaic effect in Grignard solutions is due to the formation of excited molecules by the light, either throughout the liquid or in the electrode surface layer of electrostatically strained molecules. They more or less completely replace the normal molecules on the electrode sur-face, being more or less regularly oriented. He further suggested that these molecules may or may not have the same dipole moments as in the solution, but should change the work function of the interface and give rise to a difference of potential. Dufford suggested that the most probable type of excitation is a vibration similar to that in the Raman effect, due to the independence of the

photovoltaic effect of selective adsorption, usually associated with electron displacement.

Harty's results seem to support the theory of layers of excited molecules on or near the electrode as the cause of the photopotential in Grignard solutions. An altered potential difference would result if light produces in or near these layers a number of excited molecules having different dipole moments from the normal molecules and having the property of displacing the latter from the layers until a sort of saturated layer is built up. Since the "life period" of the excited molecules may be short, the electrode "recovers" in the dark. By assuming that the "negative ends" of the polarized molecules can attach themselves to some metals and the "positive ends" to others, the positive and negative voltage and current responses can be explained. The depolarizer probably disturbs this layer of excited molecules on or near the electrode surface. The effect would probably depend on the electrodes, electrolytes, and depolarizers. Harty suggested the need for more information on the reactions involved and especially on the structure of the molecules.

Nga (III-25) studied the photopotentials of various organic molecules and concluded that only those having a group with one or more nitrogen atoms such as amines, amides, oximes, and semicarbazones showed "instantaneous" photopotentials. She (III-24) found that the meta-iodoaniline derivatives always had greater photopotentials than the ortho derivatives, the para compounds having about the same values as the meta. She (III-23) further found that 1,2-naphthalenediamine was distinctly less photosensitive than the 1,8- and 2,7-compounds, which were about equally sensitive.

Summary on photovoltaic cells of Type III

The best explanation for the photopotential produced by this type of cell seems to be the formation of excited molecules which are probably adsorbed in one or more layers at the electrode surface. These excited molecules probably change the work function of the interface of the metal and solution.

The Swensson effect, i.e., the photopotential produced by illumination of the electrolyte only, seems to be very small, as is the thermal effect. Thus for both Type II and Type III the effect appears to be photochemical.

VIII. PHOTOVOLTAIC CELLS OF TYPE IV: METAL ELECTRODES COATED WITH INORGANIC COMPOUNDS AND IMMERSED IN SOLUTIONS OF ELECTROLYTES

The cells of this type that have received the most attention are those coated with silver halide or copper oxide.

A. The silver halide cells

Becquerel (IV-31) in 1839, using silver plate coated with silver halides and immersed in dilute sulfuric acid, noted a photocurrent upon the illumination of one electrode. The current varied with film thickness, light intensity, and

color of light, the blue-violet end of the spectrum producing the greatest effect. He found the effect much greater than for uncoated metal electrodes and again concluded that the effect was not a thermal one. In the next twenty years (Becquerel IV-32 to 39) continued his work on silver electrodes coated with silver chloride, bromide, and iodide. In a study of silver silver iodide electrodes (IV-33, 34) he reported a maximum in the yellow-green range, a minimum at the beginning of the blue, and another maximum in the indigo-violet range. For silver silver chloride electrodes (IV-36) the maximum effect was at the beginning of the green region of the spectrum. However, Becquerel recognized that his light source was most intense in this spectral region, and so he studied the effects of varying the intensity as a means of determining the true color sensitivity. He also recognized the possible error due to differences of reflection and absorption of light at the electrode surface.

Griveaux (IV-75), in 1883, illuminated silver-silver bromide and silver–silver iodide electrodes and measured the *potentials*, rather than the current. He (IV-76) summarized his results as follows: (*1*) Silver–silver iodide electrodes upon illumination reach a maximum value in a certain time. (*2*) Continuous circulation of solutions of iodine of increasing concentrations in the vessel during illumination progressively decreases the maximum potential to zero, the required concentration varying directly with the intensity of illumination. (*3*) At a fixed concentration of circulating liquid and at the maximum potential, the latter gradually increases if the circulation is stopped. (*4*) The above effects are observed with silver–silver bromide or silver–silver chloride electrodes, but the concentration of the solution necessary to decrease the potential to zero depends on the nature of the sensitive salt.

Luggin (IV-97), in 1894, measured the potential (0.42 volt) produced by the exposure to diffuse sunlight of a platinum silver bromide electrode immersed in 0.1 N potassium bromide. The rate of rise of potential was found to be less for weak than for strong illumination. Continuous and intermittent light of the same mean intensity appeared to have the same effect. The potentials were lowered by previous exposures to strong light. Using the same type of cell, he (IV-98) applied a stopping potential to decrease the photocurrent to zero (called the equilibrium potential). Luggin called the current normal or positive when the action of the current was to remove halogen and cause darkening of the electrode, while currents acting in the opposite manner were called solarization currents. With silver chloride electrodes, yellow light favored the latter and blue light the former.

Scholl (IV-122, 123), in 1905, reported that platinum–silver chloride, platinum–silver bromide, and platinum–silver iodide electrodes in dilute acid or alkali halides became positive when illuminated. He stated that exposed silver iodide in aqueous salt solutions underwent dissociation, producing the ions of silver iodide and probably electrons; the latter imparted metallic conductivity to the silver iodide. The dissociation was induced by light of all wave lengths but paralleled the absorptive power of the silver iodide. Scholl's experiments indicated no change in potential on illuminating the potassium iodide solution

and showed that the solubility of the illuminated silver iodide was probably 15 to 20 per cent higher in violet light than in the dark. He considered the effect to be due to diffusion potentials.

Wildermann (I-29 to 33; II-43; IV-153) studied silver–silver halide cells and applied to them his theories of "induction periods" and "deduction periods," the law of mass action, and thermodynamic equilibrium under the influence of light. His conclusions were as follows: (1) The velocity of chemical reaction and chemical equilibrium in homogeneous systems under the action of light follows the laws of mass action. (2) The potential produced by light consists of: (a) an electromotive force due to the variation of chemical potential and solution pressure, and (b) a thermoelectromotive force. (3) The rays of all wave lengths act both "chemically" and as "heat rays," only in different amounts. (4) Reversals noted by Becquerel (IV-39) and Minchin (IV-101) are not surface phenomena but are due to polarization. (5) Each kind of equilibrium between two states of matter on exposure to light becomes shifted in the direction accompanied by the greater absorption of light.

Sichling (IV-137) studied the illumination of electrodes made by absorbing photochlorides (silver chloride and amorphous silver) in gelatin and in silicic acid and applying this paste to a platinum-gauze electrode. In potassium chloride solution positive potentials to 0.5 volt were obtained; blue and yellow light had much the same effect as white light, green light had less effect, and red light produced a negative potential. The latter may have been a thermal effect, for the temperature coefficient was found to be negative. The maximum potential increased in an approximately logarithmic manner with the light intensity.

Baur (IV-29), in commenting on Sichling's work, suggested that the increase of potential on illumination was due to the formation of the unstable photochloride Ag_2Cl, the decrease on continued illumination being caused by a change of color, whereupon the stimulating effect of the light diminished. The negative effect with red light was ascribed to the amorphous silver in the photochloride.

Iimori and Takebe (IV-83) studied silver–silver iodide electrodes in 0.3–5 M potassium iodide and concluded (1) that the potential varies with the concentration of the cell liquid according to the equation

$$E = A + B \log 1/C$$

where C is the concentration of the potassium iodide and A and B are constants depending on temperature, intensity of illumination, and the electrodes, (2) that an increase of temperature decreases the effect, and (3) that the photovoltaic effect with halide electrodes is caused by the reversible chemical reaction of silver iodide.

Athanasiu (I-4; IV-5, 8, 11, 13), in studies of silver silver halide electrodes, made the following observations: (1) The maximum sensitivity of silver iodide is at 4245 ± 20 Å. (IV-5). (2) The positive photopotential of silver iodide in neutral potassium chloride is inverted to a negative value by adding a base, the maximum sensitivity being thereby shifted to 4300 Å. (I-4; IV-13). (3) For

all cells studied, the photopotential increases when the temperature decreases, and *vice versa*, possibly owing to opposing photochemical reactions being differently affected by the change of temperature (IV-8, 13).   (*4*) The positive photoeffect reaches saturation after a few minutes of illumination with unfiltered radiation but continues to grow if the radiation is monochromatic (IV-11). (This might be due to insufficiently intense monochromatic radiation.)   (*5*) It is impossible to explain the Becquerel effect on the basis of the photoelectric effect alone (IV-8, 13).   (*6*) The results may be explained as due to the electrode functioning as an "acceptor" of the hydroxyl ion of the electrolyte. The iodine liberated by the light on the electrode may temporarily form IOH, which interferes with recombinations with the silver (I-4; IV-13).

Garrison (IV-67) coated thin sheets of silver with silver iodide by the use of vapors and by electrochemical deposition, the latter giving better uniformity of thickness. The electrolyte was saturated with silver iodide, thus fixing the ion product, but the ratio Ag^+/I^- could be varied by adding potassium iodide or silver nitrate. He drew the following conclusions: (*1*) The sign of the potential depends on the thickness or density of silver iodide. The negative effect increased with increase of the ratio Ag^+/I^- by adding silver nitrate, and the positive effect was developed by the decrease of the ratio by adding potassium iodide.   (*2*) The curves obtained by plotting potentials *vs.* intensities were of the same form, even though the negative potentials were larger than the positive ones for the same intensity.   (*3*) There seems to be no simple relation between the photopotential and the frequency. The effect seems greater in the blue and violet with a slight maximum in the yellow-green.

Garrison also assumed that light tends to separate the ions, increasing the solubility. Silver coated with silver iodide can act either as a reversible silver or as a reversible iodine electrode. Since the solubility product of silver iodide is 1.0×10^{-16}, when potassium iodide is added so that $I^- = 0.01$, then Ag^+ must be 1×10^{-14} in the dark. Hence Ag^+ could be doubled with only a slight decomposition, the I^- remaining nearly constant. Hence the silver electrode ($Ag \rightleftharpoons Ag^+ + e$) may be used to measure the silver ion increase. Thus, on adding potassium iodide the electrode would become positive, as experimentally noted. Conversely, on adding silver nitrate the electrode acts as an iodine electrode ($I_2 + 2e \rightarrow 2I^-$); the potential is negative and becomes more negative on adding silver nitrate.

Garrison (IV-68) later used silver iodide deposited on gold, platinum, and palladium plates. His results were as follows: (*1*) There is a positive effect, provided the electrode does not have silver deposited from light exposure.   (*2*) Changes of the electrolyte have little effect on the potential, for in 0.1 *N* potassium iodide solution the dark potential is 0.2587 volt, compared to 0.411 volt for the dark potentials in 0.1 *N* silver nitrate. The respective photopotentials are 0.450 and 0.432 volts.   (*3*) The relation between potential and intensity is the same as before—almost linear for low intensities and constant for high intensities.   (*4*) The photochemical action on silver iodide in any part of the visible spectrum diminishes as the light becomes more nearly monochromatic, the

light intensity being maintained at a constant value. (*5*) Illumination in the blue is necessary to sensitize the electrode to red, after which it is most sensitive in the red.

Garrison suggests that the rise of potential of the noble metal–silver halide electrodes is due to an increased number of silver iodide molecules being made polar by the light, displacing the electrons toward the halogen. His assumptions are: (*1*) There is a probability distribution of polarity among the molecules. (*2*) The greater the degree of polarity, the longer the wave length of light absorbed by the valence electrons. Thus the blue sensitizes the silver iodide to red by increasing its polarity. However, this would not seem to account for its response being greatest in red after sensitization. (*3*) The energy of light is stored in the molecule as increased polarization and thus increases the ionization and the apparent solubility. (*4*) A molecule having absorbed a quantum of energy and become polar may return to a less polar state by giving its energy to several other molecules, thus increasing their polarity.

Garrison's theory of the loosening of the ions was somewhat strengthened by his discovery (IV-69) that silver chloride, which is slightly diamagnetic, became less so, and silver bromide and silver iodide, which are slightly paramagnetic, became more so in light.

Price (IV-111) criticized Garrison's work and suggested that light formed a photohalide, accompanied by the formation of colloidal silver, which would have a higher solution pressure than massive silver, thus producing the negative effect.

Garrison (IV-70) answered Price's criticisms, showing that Price had merely reversed his calculations and thus obtained the same constant used by the author in one of his data tables. He indicated two ways in which silver–silver iodide could act as an iodine electrode: (*1*) The salt and the electrolyte retain some iodine in solution, which may ionize. (*2*) The iodide ions may be liberated directly from the crystalline lattice, the charge being conducted directly through the crystal.

$$AgI \rightleftharpoons Ag + I^- + (+)$$
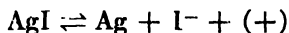
Tucker (IV-143) studied photovoltaic cells having silver halide or copper halide on platinum and on silver or copper. His work may be summarized as follows, with the note that he designated the anode as "that electrode from which current flows in the cell solution," which is negatively charged: (*1*) In cells having photosensitive substances on platinum, illumination causes oxidation of the substance if the solution is an oxidizing one, causing the exposed electrode to behave as a cathode (positively charged). If the solution is a reducing one the electrode behaves as an anode (negatively charged). (*2*) In cells of the second type, having copper halides or silver halides on copper or silver, respectively, illumination tends to promote reduction of the photosensitive substance, "local cell" action causing a reduction of the observed electromotive force, especially if the layer is not uniform. (*3*) If these "local cells" are completely reversible, the electrical behavior of the illuminated electrode is determined by the oxidizing

or reducing nature of the cell solution. (*4*) The photoeffect is in the order silver chloride > silver bromide > silver iodide, whereas the order for the photoelectric effect is iodine > bromine > chlorine, as reported by Toy, Edgerton, and Vicks (IV-141). (*5*) The results of Becquerel, Minchin, Wildermann, Case, and Garrison can be accounted for on the basis of these considerations.

Audubert (IV-14, 15, 16, 18), in a study of silver–silver halide cells, made the following observations:

(*1*) With very thin layers of silver halide, red rays give a negative charge, while blue rays initially give a higher negative charge which gradually becomes positive after several hours' exposure (IV-14).

(*2*) The effect is independent of a thermal effect and is in the opposite direction (IV-15).

(*3*) Blue radiation is much more active than red (IV-15).

(*4*) In all cases a polarization of inverse sign to that of the electrode increases the effect, while polarization of the same sign decreases it but never reverses it (IV-15).

(*5*) Experiments with buffered solutions confirm the statement that lowering the pH raises the positive photopotential and increasing the pH raises the negative potential (IV-18).

(*6*) The photoeffect diminishes when the concentration of cation is raised (IV-18).

(*7*) The photoeffect is attributed to the photolysis of water and the displacement of the resulting equilibrium by the photosensitive substance. The sign of the photopotential is negative or positive, depending upon the way hydrogen or oxygen displaces the electrochemical equilibrium (IV-18).

Goldmann (II-7) reported observations of the illumination of silver–silver chloride and silver–silver bromide electrodes in sodium chloride and sodium bromide solutions, respectively. He claimed that Wildermann's (I-30, 31, 32) hypothesis that such cells have a definite electromotive force determined by the light intensity is wrong; he suggested that selective absorbing molecules send off electrons into the solution, allowing the rest of the solution to give its positive charge to the electrode. Later, Goldmann (II-8, 9) reiterated his theory that the primary process in a photochemical process is a removal of electrons and that the Becquerel effect is analogous to the Hallwachs–Leonard photoelectric effect. He explained that solarization was a kind of polarization of the photoelectric elements, taking place when the charges appearing are not neutralized, and that it could be avoided by the use of oxidizing substances at the electrodes.

Experiments by Fajans, Frankenburger, Fromherz, and Karagunis (IV-51, 52, 53, 54, 62, 63, 64) indicated that the interaction between light and silver bromide was influenced by adsorbed ions. Fajans (IV-50, 51, 54) suggested that under the influence of the adsorbed silver ion the amount of energy required to transfer an electron from a bromide ion to a silver ion may be decreased. However, in the case of silver iodide, he asserted that one is dealing not with a change in the energy requirements but simply with an increase in the number of elementary processes. If the surface were coated with silver ions, then an

equal amount of silver iodide would absorb a larger portion of the incident light
and therefore more silver iodide would be decomposed. He concluded that one
may therefore regard the silver ion not only as a chemical acceptor but also as a
spectral sensitizer in the photolysis of the silver halides. The primary action
of light on silver bromide is ejection of an electron from the bromide ion to the
silver ion, forming neutral atoms of silver and bromine.

Sheppard and coworkers (IV-127 to 135, 147), in a study of the silver–silver
halide electrodes (IV-147), concluded that Tucker's theory of initial negative
photopotentials caused by local cell reactions on the illuminated electrode may
be discarded. The precision of their work, their recognition of variables, and
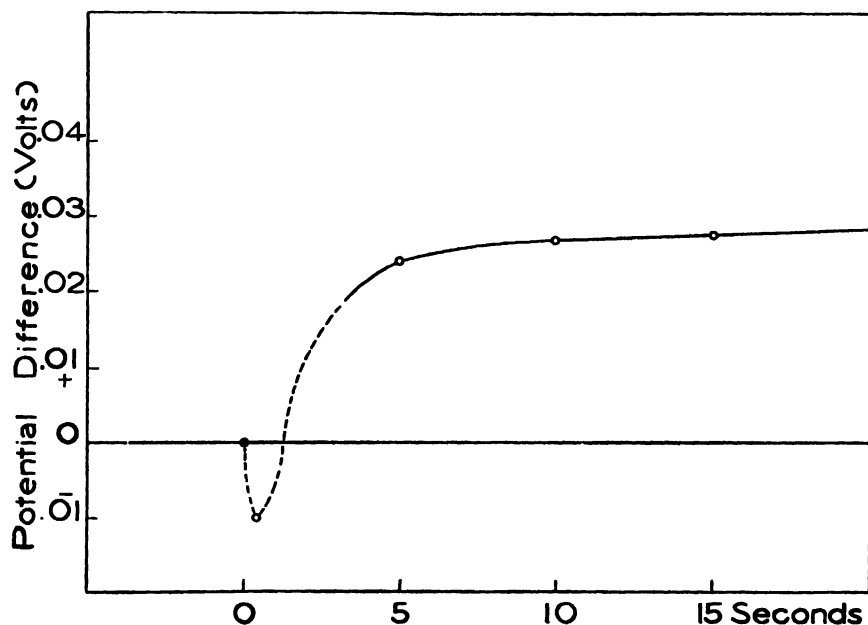
Fig. 2. Typical potential-time curves, using a vacuum-tube voltmeter. Silver–silver
bromide electrodes; silver bromide thickness = 0.00039 mm.; photocell electrolyte, KBr
saturated with AgBr; radiations, complete spectrum of quartz mercury arc.

the testing and control thereof seem to be the best of the experimental work on
the photovoltaic effect for this type of cell. To obtain rapid measurement in
the first fraction of a second of exposure of a cell to light they used an amplifier–
oscillograph system. Figure 2 shows a typical potential–time curve using a
vacuum-tube voltmeter; it shows that the nearly inertialess negative effect is
still observable after five 0.01-sec. exposures. The quasi-instantaneous negative
portion probably was not eliminated on the appearance of the positive effect,
but the observed potentials are the resultants.

They report the following conclusions from their work on silver–silver bromide
electrodes: (1) As the thickness of silver bromide increases, the photopotentials
assume a more steady potential after the first 30-sec. exposure and remain

steady for at least 90 sec. (*2*) The thinner the silver bromide layer, the more marked the initial negative effect. (*3*) The time to obtain the maximum negative potential is about 0.06 sec. in all cases. (*4*) The maximum difference of potential increases with age at least for the period 2 min. to 8 days. (*5*) This change over a period of time may be due to a change in crystal structure or to removal of hydrogen bromide or bromine formed during electrolysis. (*6*) There is no Swensson–Becquerel effect on illuminating the solution (IV-132).

Sheppard and Vanselow (IV-147) propose the following theory: The primary photochemical process may be represented by

$$Br^- + h\nu = Br^* + e$$
$$Ag^+ + e = Ag$$
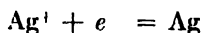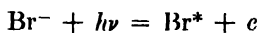
Both the electrons and the bromine atoms or molecules may be supposed to move in the direction of the light ray toward the silver electrode, the former producing the initial negative surge by an increase in electron pressure. When the more slowly moving bromine reaches the electrode, it reacts to give a positive potential

$$\tfrac{1}{2}Br_2 + Ag \rightarrow Ag^+Br^-$$
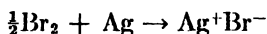
so the mechanism may be represented by
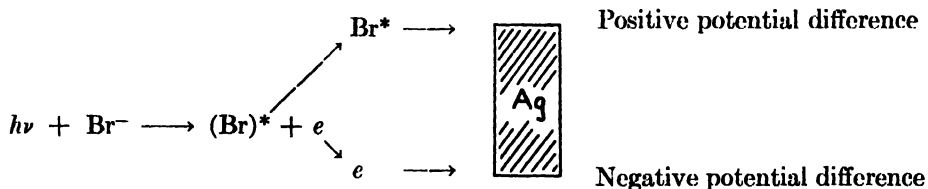
Indications that this is the correct mechanism are the following: (*1*) The relation of the fall of the positive potential with time on removing illumination is in agreement with the diffusion resistance being directly proportional to the thickness of silver bromide. (*2*) Oscillograph and intermittent-exposure data demonstrate the inertialess character of the negativation. This is the order obtained in photoconductance of crystals. (*3*) Halogen acceptors, such as sodium nitrite or acetone semicarbazone, eliminate or reduce the positive effect, as shown in figure 3 (as predicted). (*4*) An increased positive potential is produced in the dark by permitting bromine to diffuse through the silver bromide of one electrode, the other being shielded by an alundum crucible.

Sheppard suggests the two possible reaction schemes:

	I		II
(1)	$Br^- + h\nu \rightarrow (Br^-)^*$	(1)	$Br^- + h\nu \rightarrow (Br^-)^*$
(2)	$(Br^-)^* \rightarrow Br + e^*$	(2)	$(Br^-)^* + Ag^+ \rightarrow Ag + Br$ or Br^*
	$Br^* + e$		
(3)	$Ag^+ + e \rightarrow Ag$	(3)	$Ag + Br \rightarrow Ag^+ + Br^-$
(4)	$Br + Br \rightarrow Br_2$		
(5)	$Ag + Br \rightarrow Ag^+Br^-$		

Sheppard provisionally accepts scheme I as more probable. Evidence for the production of relatively free internal photoelectrons in insulated silver halide has been given by Arrhenius (IV-1, 2), Scholl (IV-122, 123), and Gudden and Pohl (IV-77).

Assuming the reaction to be

$$\tfrac{1}{2}Br_2 + Ag \rightleftharpoons Ag^+Br^-$$
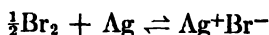
For equilibrium

$$K = \frac{(Br_2)^{1/2}(Ag)}{(Ag^+Br^-)} = \frac{[Br_2^-]^{1/2}[Ag]}{[Ag^+][Br^-]}$$
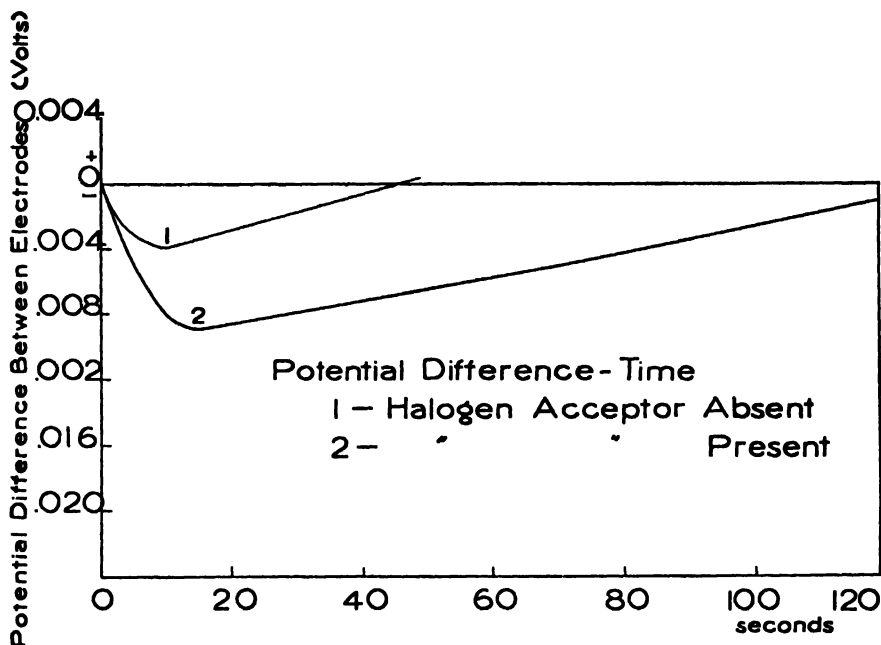
Fig. 3. Effect of halogen acceptors

Since [Ag] and [Ag⁺Br⁻] are constant,

$$K = k(Br_2)^{1/2}$$

and from Nernst's equation

$$E = E_0 - RT \log k[Br_2]^{1/2}$$

A plot of steady E.M.F. against log $(Br_2)^{1/2}$ is a straight line, until the lowest concentrations are reached.

Sheppard and Vanselow (IV-130), after considering the energy steps in the Born cycle for calculating lattice energies of silver halides, conclude that photolysis of solid silver halide may occur directly to give halogen and silver or may occur indirectly by way of separation of electrons from halide ions, followed

by acceptance of electrons by silver ions. They assume that both the lattice energy and the electron affinity are lowered at interfaces, making it possible for the inner photoelectric effect to take place in the visible spectrum.

Herzfeld (IV-80) has calculated the influence of the surroundings on the work required to transfer an electron from the bromide ion to the silver ion in the silver bromide crystal. Sheppard and his associates (IV-133, 134, 135) have studied the effect of adsorbed acidic and basic sensitizing dyes on the photolysis of silver halides (this will be discussed in a later section). From present results it cannot be concluded whether the electrons are initially released from the dye by absorption of light and recovered from bromide ions of the crystal with release of bromine, or whether the dye merely transmits sufficient energy to the crystal to separate electrons and halogen. Sheppard (IV-135) also reported new values of 0.09 sec. as the time to reach the initial maximum negative photopotential and 1.23 sec. to recross the zero potential line. This work was done with an Einthoven string galvanometer with a direct-current vacuum-tube amplifier (IV-148).

Kieser (IV-91) believes that the photolysis of silver bromide according to the theories of Fajans explains regression, coagulation, the photovoltaic effect, and photoelectric conductance of the silver halides over the entire visible spectrum. He finds that the maximum photoelectric conductivity corresponds with the greatest photochemical sensitivity. He also affirms the hypothesis of Fajans and of Sheppard and Trivelli.

Winther (II-44) has concluded that (1) effective photovoltaic electrodes have large surface area, have a corresponding absorptive power, and are made more conductive by irradiation, (2) the effect depends on a primary ionization and a consequent change in the absorption equilibrium, and (3) the often-observed chemical processes are secondary side reactions.

Kirillow and coworkers (IV-92, 93) reported a study of the irradiation of pure monocrystalline silver chloride, silver-silver iodide, and gold-silver iodide electrodes. They interpreted the effects as photochemical rather than barrier-film effects, and offered a mechanism on the basis of the hypothesis of Fajans and of Sheppard and Trivelli.

Hartung (IV-78), using a microbalance, reported a change of weight of illuminated silver bromide, silver chloride, and silver iodide, indicating decomposition into silver and free halogen. Strömberg (IV-139), from a similar experiment with silver bromide, ascribed the loss of weight to thermal effects. Mutter (IV-106), Schwarz and Stock (IV-124), and Steiner (IV-138) have contributed data indicating that the photolysis of silver bromide and of silver chloride liberates halogen. Feldmann and Stern (IV-55, 56, 57) have used a potentiometric method to follow the splitting of chlorine or bromine from silver chloride or silver bromide during illumination, using a nitrite as a halogen acceptor. They found a quantum yield approaching 1 for precipitated silver chloride at 3130 Å. and 3650 Å. in the presence of nitrite, and for precipitated silver bromide at 3650 Å. and 4360 Å. Jouaust (IV-85) found that the maximum light sensitivity of silver iodide cells was at 4245 Å., independent of the electrolyte.

Kameyama and Kikuchi (IV-87) calculated the long-wave-length limit of dissociation of silver halides by the method of de Boer as applied to alkali halides. They found that the energy for an electron to pass from the halide ion to the silver ion and for the silver halide to be adsorbed by the lattice was 3250 Å. for silver chloride and 1100 Å. for silver bromide. The existence of crystal effects was thought to make possible photolysis at longer wave lengths of 3900 Å. and 4350-4600 Å., respectively. Trillat and Motz (IV-142) found crystalline silver

TABLE 3

Spectral sensitivity of silver–silver iodide electrodes

WAVE LENGTH	PHOTOPOTENTIAL POTENTIAL/LIGHT INTENSITY
Å.	
5460	0
4358	30.9
4046	66.1
3660	54.2
3341	54.2
3130	40 6
3025	34.2
2967	31.9
2652	30.3
2536	38.75

TABLE 4

Spectral sensitivity of silver and of silver–silver bromide electrodes

WAVE LENGTH	PHOTOPOTENTIAL OF SILVER–SILVER BROMIDE ELECTRODES IN 0.001 *M* KBr	PHOTOPOTENTIAL OF SILVER ELECTRODES IN 0.001 *M* KBr
Å.	*millivolts*	*millivolts*
6908	0.4	0.0
6234	0.1	0.0
5780	1.6	0.0
5461	2.8	0.1
4916	0.3	0.0
4358	3.6	0.5
4047	5.2	3.6
3650	5.5	4.2

on the overexposure of silver bromide–gelatin emulsion. All these data lend support to the theory of Fajans and of Sheppard.

Sanders and Kolthoff (VI-16) reported that silver bromide showed a photovoltaic effect even in the absence of all free metal. They found that the photovoltaic effect of pure silver bromide was always negative, in contradiction to prior work with metal–silver halide electrodes. Previously reported photopotentials of silver–silver halide electrodes were regarded to be complex functions of the effect, plus the oxidizing action of free halogen or hypohalite on the metal. According to Sanders and Kolthoff, the most probable mechanism for the photovoltaic effect at metal-free silver bromide is a photodecomposition resulting in

the liberation of a free bromine atom and an electron. The electron may then react to produce silver atoms or take its place in the lattice, in either case playing no rôle in the potential change, since the system is non-metallic. The free bromine can diffuse into the solution and hydrolyze, giving hypobromite and bromide ions.   These bromide ions give the silver bromide salt its negative potential. The fact that positive photopotentials are never observed is due to the absence of free metal which may be oxidized by the bromine or hypobromite.

The spectral sensitivities of silver–silver iodide electrodes, as determined by Athanasiu (IV-5), are given in table 3 and for silver–silver bromide electrodes, as determined by Clark and Garrett (IV-47), are given in table 4.

B. *Copper oxide photovoltaic cells*

Hankel (I-19), in 1877, discovered that partially oxidized copper in water became negative on illumination. As the thickness of the oxide layer was increased, the potential became less negative and finally became strongly positive, blue and violet light producing the greatest effect. He showed that the effect was not a thermal one. Pellat (IV-108), in 1879, reported that a Daniell cell in which the copper plate was oxidized produced a lower potential, about 0.029 volt lower, when placed in sunlight but that if the positive plate were coated with an oxide by heating in a Bunsen flame, light increased the E.M.F. by making the anode more positive.

Gouy and Rigollot (IV-73), in 1888, found that a copper–copper oxide electrode in a solution of a metallic chloride, bromide, or iodide was very sensitive to light, even of low intensity. The cuprous oxide coating was more sensitive than cupric oxide. A positive potential of several hundredths of a volt was reported for illuminating copper–copper oxide plates in sodium chloride solution with diffuse sunlight and at least 0.1 volt with direct sunlight. Rigollot (IV-118) found the maximum in the sensitivity curve of copper–copper oxide electrodes in sodium chloride was at 5000 Å., in sodium bromide at 4850 Å., and in sodium iodide there was a broader maximum at about 5300 Å. The current was found to be proportional to the intensity of illumination except for intense illumination, where the curve flattened. Rigollot (IV-119) also found that the change in potential on illumination was eight times as large in 1 per cent potassium iodide as in 1 per cent sodium nitrate. In changing from a 0.5 per cent solution of potassium sulfate to a 10 per cent solution the sensitivity increased 300 per cent, but for sodium iodide it decreased 80 per cent. Rigollot (IV-115) noted an increased sensitivity when the copper–copper oxide electrodes were dyed with eosin, erythrosin, safranine, malachite green, and Soluble blue.

Goldmann and Brodsky (IV-72) studied oxidized copper electrodes in chlorides, bromides, sulfates, and nitrates of alkali and alkaline-earth metals. The "photoelectric characteristic" was independent of the concentration of sodium chloride in the range 0.05 N to 1.0 N and of the nature of the electrolyte for the above compounds. The photocurrent decreased on prolonged or repeated strong illumination. The ratio of the current to light intensity decreased with increasing intensity but remained about proportional to the intensity when the

solution was stirred. The current increased when the temperature was increased.

Case (IV-44), using the cell

Cu | CuO | NaCl solution | Cu
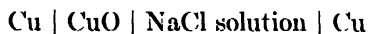
obtained a current of 0.5 milliampere at 0.1 volt upon illuminating the oxidized electrode. Later (IV-45) he found that the cuprous oxide electrode in formic acid acted as an anode to produce a potential of 0.11 volt; upon continuous illumination the potential dropped nearly to zero, but on rotation of the electrodes so that they were alternately illuminated, a continuous alternating current was produced for 500 hr., without noticeable disintegration of the light-active material.

Case considered the cuprous oxide to be oxidized under the influence of the light to cupric oxide, which dissolves to form copper formate, this action continuing until the cuprous oxide is exhausted and the current goes to zero. On immersing polished copper in copper formate in the dark, a coating of cuprous oxide is formed. Reversing the plates gives the original condition, i.e., the cuprous oxide is oxidized to cupric oxide and the copper in contact with copper formate forms cuprous oxide.

Von Samsonow (IV-150) studied the action of depolarizers on oxidized copper electrodes immersed in sodium sulfate, bromate, iodate, and chlorate solutions. The depolarizers were ferrous sulfate and oxalate, glycine developer, p-aminophenol and sodium sulfide, sodium arsenite, and sodium phosphite. The potentials were higher in iodate and bromate than in sulfate and chlorate solutions.

Garrison (IV-65, 66), in an extensive study of cuprous oxide electrodes, obtained the following results:

(1) A cuprous oxide electrode which is positive on illumination may be changed to negative by increasing the density of the oxide coating.

(2) The current produced by the light flows in such a direction as to destroy the illuminated oxide film.

(3) An electrode having a negative effect on illumination in a neutral electrolyte may be made to have a positive effect by increasing the hydrogen-ion concentration, and vice versa.

(4) With electrodes having a negative light effect, increase in cupric-ion concentration reduces the negative effect but does not produce a positive effect.

(5) The initial maximum negative photopotential is approximately proportional to the intensity of the light for low intensities but beyond a certain intensity is constant. With increasing intensity the positive effect increases as the logarithm of the intensity.

(6) With electrodes showing both positive and negative effects, light of long wave lengths produces a negative effect, while light of short wave lengths produces a positive one.

(7) The conductivity of a suspension of cuprous oxide in pure water is not influenced by white light, but the conductivity of a suspension of copper coated with a thin layer of cuprous oxide is increased. This has been distinguished from

a temperature effect and is explained by assuming cuprous oxide to be more soluble in light.

Garrison explained the photovoltaic effect on the basis of light increasing the solubility of cuprous oxide and shifting the equilibrium of the reaction:

$$Cu_2O \text{ (solid)} \underset{}{\overset{light}{\rightleftharpoons}} Cu_2O \text{ (dissolved)} \rightleftharpoons 2Cu^+ + O^{--}$$
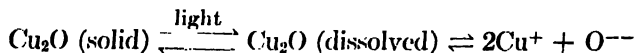
A positive photopotential results when the electrode potential is determined by the reaction

$$Cu^+ \rightleftharpoons Cu - e$$
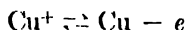
and a negative potential results when the potential is determined by the reaction

$$2O^{--} \rightleftharpoons O_2 + 2e$$
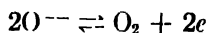
Garrison concludes, "If we start with the assumption that light causes an increase in the solubility of cuprous oxide, then all the characteristics of the influence of light which have been found for these cells may be explained by the established laws of electrochemistry. The influence of the radiation in such cases is primarily the separation of the charged elements as ions followed by the establishment of an electrochemical equilibrium. In some instances the limit of solubility from an electrochemical standpoint is reached and a spontaneous discharge of ions takes place with the liberation of the elements."

Van Dijck (IV-144) studied cupric oxide electrodes in solutions of potassium nitrate, zinc nitrate, and sodium bromate with illumination of 4490-8500 Å. and found the "stopping potential" to be the same for all wave lengths. He concluded that the effect does not consist in the neutralization of positive ions in the liquid by electron ejection from the electrode, as had been proposed by Goldmann. Van Dijck later (IV-145) reaffirmed this conclusion and proposed that, under the action of light, cupric oxide is decomposed into copper and oxygen and that the copper reacts with the cupric oxide.

$$2CuO \underset{}{\overset{light}{\rightleftharpoons}} 2Cu + O_2$$

$$Cu + CuO \rightleftharpoons Cu_2O$$

$$4Cu + O_2 \rightleftharpoons 2Cu_2O$$

$$2Cu_2O + O_2 \rightleftharpoons 4CuO$$
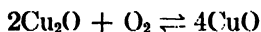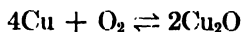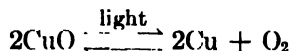
Tucker (IV-143) studied copper–cuprous oxide and platinum–cuprous oxide electrodes, using both gauze and sheet metals. He concluded that the cell solution, the nature of the metal, and "local cells" were the important factors. The "local cell" action was at a minimum for a thick or uniform layer of the light-sensitive substance and less for the sheet type than for the gauze. He found that in all reducing solutions, photochemical reduction of cuprous oxide to copper tends to take place, and in oxidizing solutions oxidation to cupric oxide tends to take place on the illuminated electrode, as postulated by Bancroft (IV-27).

Winther (IV-156; VII-29) explains the photoeffect of the cupric oxide electrode on the basis of copper acting as an oxygen electrode with an oxygen pressure far smaller than that at the surface of the oxide layer. On irradiation the cupric oxide becomes a conductor, the whole forming a concentration cell. Winther (IV-157) later added to the support of the effect as a "photoelectric conductivity" phenomenon by showing a proportional increase of conductivity of the oxide film with light intensity.

Lanyi and Theisz (IV-96) studied silver, copper, silver oxide, and cupric oxide electrodes in distilled water and in dilute solutions, both with and without foreign gases bubbled through the solutions and over the electrodes. The pure metals showed effects up to 1 millivolt, while the oxidized surfaces showed effects up to 200 millivolts. Hydrogen, nitrogen, and oxygen were without effect. Lanyi and Theisz explained the effect as due to a photochemical reaction between the electrode and solution which is reversible in the dark.

Karshulin (IV-88, 89) studied cupric oxide electrodes in sodium halide solutions and in water. With the latter there was little rise in potential; hence he concluded that there was no decomposition of the cupric oxide in light in the presence of water. The purely photoelectric interpretation was rejected, for the effect did not disappear with positively charged static electrodes. The effect was attributed to photochemical and autocatalytic processes.

Fink and Alpern (IV-59) were interested in the engineering development of photovoltaic cells and particularly for the cell

$$\text{Cu} \mid \text{Cu}_2\text{O} \mid \text{Pb(NO}_3)_2 \mid \text{Pb}$$
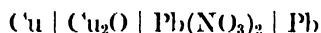
They found a sensitivity of 150 microamperes per lumen, a maximum response at 4600 Å., and a linear relation between current and illumination for the range 0 to 100 lumens per square foot.

Fink and Fogle (IV-60) compared solid cells with liquid photovoltaic cells under varied conditions. Fink and Adler (IV-58) studied the cell

$$\text{Cu} \mid \text{Cu}_2\text{O} \mid 1 \text{ per cent Pb(NO}_3)_2 \text{ solution} \mid \text{Pb}$$
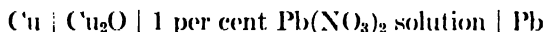
under widely varying conditions and found three types of relation between the potential and the intensity of illumination. In the region of small intensities, below 10 lumens per square foot, the potential varies linearly with intensity; in the region of 10 to 100 lumens per square foot, the potential varies as the logarithm of the intensity, while at still higher values it approaches a saturation value. They explained this form of functional dependence by an application of the theory of absolute reaction rates.

Kato and Hayami (IV-90) determined the time effect of the photovoltaic effect and the change of weight of cupric oxide when exposed and unexposed. The decrease of the weight of cupric oxide on exposure was considered to be proof that the photovoltaic effect was due to a photochemical change, rather than to photoelectric emission. Hayami (IV-79) later studied the cells

$$\text{Cu} \mid \text{Cu}_2\text{O} \mid \text{CuO} \mid 0.1 \, N \text{ NaOH} \mid 3 \, N \text{ NaOH} \mid 0.1 \, N \text{ KCl, Hg}_2\text{Cl}_2 \mid \text{Hg}$$

and

$$Cu \mid Cu_2O, CuO, 0.1 \ N \ NaOH, HgO \mid Hg$$
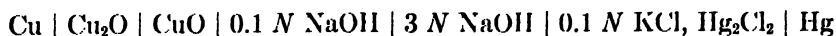
and attributed the effect to the photoreversible reaction:

$$2CuO \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} Cu_2O + \tfrac{1}{2}O_2$$
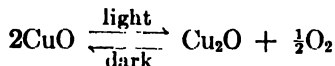
From thermodynamic calculations on the reaction system, the equilibrium constants in light and dark were in good agreement with experimental data.

Meserve (IV-100) studied the photovoltaic properties of the cell:

$$Cu \mid Cu_2O \mid Pb(NO_3)_2 \ (1 \ \text{per cent}) \mid Cu_2O \mid Cu$$
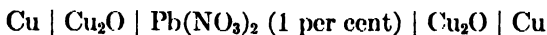
and found that the spectral sensitivity with sinusoidally interrupted light of variable frequency checked with that of steady illumination. A similar cell, except that the electrodes were separated by a gel containing a conductive aqueous salt solution such as lead nitrate, was patented by Wilson (IV-154).

Kalita (IV-86) found that with a copper strip coated with a layer of cuprous oxide and exposed to light while being cathodically polarized in aqueous potassium chloride, the cuprous oxide layer decomposed with the separation of copper on the illuminated area. The course of the process was concluded to be:

$$Cu_2O \rightarrow 2Cu + O$$

The rôle of the polarization depends on the removal of oxygen according to the equation:

$$O + H_2O + 2e \rightarrow 2OH^-$$
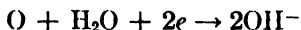
Sheppard and Vanselow (IV-131), from their experiments with silver halide cells, suggested that the primary process of copper–cuprous oxide cells is analogous, —a transition from an internal photoelectric effect to an external one. However, the succeeding process is hindered by the rectifying layer between copper and cuprous oxide.

Athanasiu (IV-5, 8, 9, 10, 13), in his studies of copper–copper oxide cells, reported as follows: (1) The maximum sensitivity of cupric oxide is at 4046 Å. and the minimum at 3100 Å. (IV-5, 9). (2) The sensitivity of the electrodes in potassium chloride, sodium chloride, and sodium bromide diminishes in that order (IV-5). (3) The potential increases when the temperature decreases and vice versa, probably because opposing photochemical reactions are differently affected by a change of temperature (IV-8, 13). (4) The presence of cupric oxide in admixture with cuprous oxide displaces the maximum of the sensitivity curve toward the red and diminishes the potential produced by the light (IV-9). (5) The barrier-film hypothesis, as suggested to explain the behavior of the dry cuprous oxide cell, cannot give a general explanation of photovoltaic phenomena, especially where there is reason to suspect photochemical action with intervention of the electrolyte (IV-10). (6) The positive photovoltaic effect is increased by a decrease in pH and is decreased or reversed by increase of pH (IV-13). (7)

It is impossible to explain the photovoltaic effect on the basis of the photoelectric effect alone (IV-13).

Audubert (IV-15 to 23; V-1) has been one of the chief exponents of the theory of photolysis of water in the photovoltaic effect. Some of his results with copper cuprous oxide electrodes are as follows:

(1) A polarization of inverse sign to that of the electrode increases the effect, while a polarization of the same sign decreases but never reverses it (IV-15, 16).

(2) Only very slight or no photopotentials are obtained under anhydrous conditions. Slight photopotentials are always obtained with solvents difficult to dehydrate and with porous electrodes. Studies were made of copper oxide cells

TABLE 5

Spectral sensitivities of copper-copper oxide electrodes

WAVE LENGTH	PHOTOPOTENTIAL*	POTENTIAL/LIGHT INTENSITY†
Å.	*millivolts*	
6908	15.0	
6234	2.0	
5780	20.0	
5461	30.0	
4916	7.5	
4386		6.5
4367		8.6
4359	24.0	
4348		11.0
4324		14.5
4301		16.6
4282		19.0
4258		21.0
4236		19.9
4216		16.6
4197		12.5
4047	41.4	
3650	41.2	

* Clark (I-14).
† Athanasiu (I-4).

in different solvents such as acetone, ether, ethyl alcohol, and methyl acetate, rendered conducting by sodium iodide. Light appears to displace the oxidation-reduction equilibrium by photolysis of water (IV-17, 21).

(3) Photoconductance is not an essential factor in photovoltaic effects. The maximum photovoltaic effect for cuprous oxide is at 4000 Å., but the maximum photoconductance is at 5000 Å. Furthermore, the influence of variation of light intensity on the two effects is very different (IV-23).

(4) An increase in pII increases the negative photopotential and a decrease in pII increases the positive photopotential. Increasing the cation concentration decreases the photovoltaic effect (IV-18).

(5) The photovoltaic effect is attributed to the photolysis of water and the dis-

placement of the resulting equilibrium by the photosensitive substance (IV-17, 18, 21, 22).

(6) A copper–cuprous oxide electrode shows a positive photopotential with a maximum at 4000 Å. in most electrolytes, particularly reducing agents, but a weak negative potential with a maximum at 6200Å. in an oxidizing medium. By choosing the proper electrolyte, photoelectrochemical effects can be dissociated from secondary electronic effects; under some conditions they may be superposed (IV-19).

(7) The potential of copper–cuprous oxide electrodes in solutions of copper sulfate depends on the equilibrium between the cupric and cuprous ions and on an oxidation-reduction process (IV-19, 20).

$$E = E_0 - \frac{RT}{2F} \log [Cu^{+1}]$$

Pastel (IV-107) studied copper–cuprous oxide electrodes in distilled water and in sodium chloride solution and concluded that water played an essential rôle; the hydroxyl ions were regarded as responsible for the reaction causing the potential. Theodoresco (IV-140) confirmed earlier reports that a negative polarization increased the positive potential of the copper–cuprous oxide electrode, while positive polarization decreased it. She concluded that the effect was due to a displacement of the oxidation-reduction equilibrium, probably by photolysis of water.

In recent years there have been some suggestions that the copper oxide photovoltaic cell closely resembles the dry "barrier-layer" type of cell. Barton (IV-28) has pointed out that the three photoeffects—change in resistance, change in potential, and photoelectric effect of cuprous oxide—begin at increasingly shorter wave lengths in the order mentioned, indicating that the least energy is required to excite electrons, a greater amount is necessary to remove an electron, and the greater the dielectric constant of the medium the less is the amount of energy needed to remove the electrons. Duhme (IV-49) concluded that the physical interpretation of the photoelectric effect in a rectifying layer in photovoltaic cells is supported by the behavior of cuprous oxide photoelectric cells. Waibel (IV-151) concluded that all the characteristics of barrier-film photocells occur also with cuprous oxide electrodes in a 5 per cent potassium chloride solution.

Müller and Spector (IV-105), in a study of copper-cuprous oxide electrodes in sodium chloride, potassium chloride, or a mixture of the two, found that the primary function of the electrolyte is to act as a conductor for the photoelectric current, although secondary chemical effects do arise. They suggested that a new avenue of approach to the solution of the photovoltaic problem has been opened by the advent of the barrier-layer cell of Lange (VII-18) and Schottky (VII-23). Griffith and Boucher (IV-74) found that upon irradiating with x-rays a "barrier-layer"-type cell of cuprous oxide and a liquid photovoltaic cell, using cuprous oxide electrodes in 0.34 N sodium chloride, comparable currents were obtained.

Roulleau (IV-120, 121) noted a maximum at 3900 Å. and a second maximum

at 4700–4800 Å., due to superposing the photoelectronic and photochemical effects upon illuminating a copper cuprous oxide electrode with a blocking layer and immersed in an electrolyte. Their results point to the predominance of the photoelectrochemical explanation; the photoelectronic effect disappears if care is taken to clean the surface and so to remove the "barrier layer."

Miseliuk (IV-103) regarded the photovoltaic effect as a barrier-layer phenomenon associated with polarization of the surface. Fink and Fogle (IV-60) found that the wet type of cuprous oxide photovoltaic cells depended on electrolytic action for generation of a current, whereas the solid cuprous oxide cell converted luminous energy directly into electrical energy. Therefore, they concluded that the primary action of the solid type was distinctly different from that of the wet type.

C. Metal–metal sulfide photovoltaic cells

Laur (VII-19) found in 1881 that in a cell of

$$Ag \mid Ag_2S \mid NaCl, CuSO_4 \text{ (solution)} \mid Hg \mid Pt$$

the silver sulfide became more positive on illumination. Bidwell (IV-41) reported that silver-silver sulfide electrodes were very sensitive to light, but that copper–copper sulfide electrodes were not. Chaperon and Mercadier (IV-46) noted an instantaneous effect on illuminating silver-silver sulfide electrodes in an electrolyte. Rigollot (IV-116) irradiated silver-silver sulfide electrodes in dilute salt solutions with infrared rays and found the illuminated plate always to be negative, an effect which he concluded could not be thermal.

Athanasiu (I-4; IV-8, 10, 11), in a study of silver-silver sulfide cells, reported (1) that the photovoltaic effect of silver electrodes thickly coated with silver sulfide is negative, (2) that the sign and magnitude of the effect can be changed by modifying the pH, and (3) that the photovoltaic potential increases when the temperature decreases.

Audubert (IV-22, 23) found the maximum photovoltaic effect of silver sulfide to be 10,000 Å. and the effect to be only slight or zero in non-aqueous electrolytes.

Athanasiu (IV-3, 4) found that the photopotential of mercuric sulfide was negative, with a maximum response at 4046 Å. Audubert and coworkers (IV-22, 26) reported that the cadmium sulfide electrode has a photopotential which was generally negative, and especially high in oxidizing solutions but the opposite in reducing solutions. The electrode showed maxima at 3900 Å. and at 5200 Å. with a minimum at 4100 Å. Audubert concluded that the effect was due to photolysis processes.

Fischer, Gudden, and Treu (IV-61), in 1937, found that various kinds of lead sulfide immersed in electrolytes and irradiated with light exhibited currents which were proportional to the light intensity and which were regarded to be photoelectric rather than thermionic. Schröppel (VII-24), in 1938, reported the quantum yield in photovoltaic cells of lead sulfide to be 0.03, and in those of silver sulfide to be 0.2, while antimony sulfide gave no reproducible results.

D. Miscellaneous types of coated-electrode cells

Athanasiu (I-4; IV-3, 4, 8, 11) found that light increased the potential of

$$Hg \mid Hg_2F_2, \quad Hg \mid Hg_2Cl_2, \quad Hg \mid Hg_2Br_2, \quad \text{and } Hg \mid Hg_2I_2$$
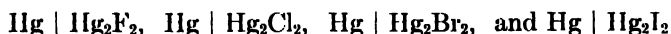
increasing in the order named. The maximum sensitivities for the chloride, bromide, and iodide were at 2536, 2967, and 4046 Å., respectively. The effects of change of pH and temperature were similar to those discussed for other electrodes. Audubert (IV-17) found only a slight effect or no effect for mercurous and cuprous iodides in non-aqueous electrolytes. Rao (IV-113) studied the photovoltaic

TABLE 6
Spectral sensitivities

WAVE LENGTH	PHOTOPOTENTIALS* METAL-METAL HALIDE			POTENTIAL/LIGHT INTENSITY METAL METAL SULFIDE	
	Mercurous iodide	Mercurous bromide	Mercurous chloride	Mercuric sulfide*	Cadmium sulfide†
Å.					
7000					7.0
6000					30.0
5460	0	0		0.5	
5200					48.0
5000					10.0
4916	20.0	0			
4358	35.0	0		3.1	
4046	39.2	4.9		3.8	
4000					25.0
3660	35.0	8.1	0	3.3	
3130	30.1	42.0	1.7	2.9	
3025	25.4	44.9			
2967		50.5	7.8		
2652	32.9	44.1	27.2		
2536	28.0	35.0	38.5		

* Athanasiu (IV-4).
† Audubert and Stora (IV-26).

properties of eleven phototropic mercury compounds and found that short wave lengths produced the maximum potential. Dyeing electrodes with erythrosin increased the potential and shifted the maximum towards the red. The photovoltaic effects of cuprous chloride, fluoride, and iodide have been studied by Audubert and Lebrun (IV-20, 22). Copper iodide in copper sulfate, nitrate, and chloride was studied by Quentin (IV-112), who found that the effect depended on the action of light on the liquid as well as on the electrode.

The photovoltaic effect of an aluminum–selenium electrode in euanthol was noted in 1895 by Minchin (IV-102); the cell was most sensitive in the yellow region. Swinton (VII-26) noted that an illuminated copper–selenium electrode in tap water became negatively charged. Audubert and Roulleau (IV-24, 25)

discovered that the photovoltaic effect of platinum–selenium electrodes was positive, of the same order of magnitude in non-aqueous as in aqueous solutions and less in a reducing solution than in an oxidizing medium. They considered the mechanism to be photoelectric and not photoelectrochemical.

Cochn and Mykolajewycz (IV-48) explained the photoeffect of bismuth oxide electrodes in terms of reduction of Bi_2O_4 to Bi_2O_3 under the influence of light.

Grube and Baumeister (VII-16) found that platinum platinum oxide in sulfuric acid showed a decrease in potential on exposure to light. The influence of x-rays was similar to that of light.

Pougnet and coworkers (IV-110), in 1913, noted that the potential of a Weston cell in a quartz vessel decreased from 1.0252 to 1.0192 volts when illuminated with a mercury-vapor lamp. The slowness of recovery, about 40 min., indicated a chemical rather than a physical effect.

Young and Pingree (I-34), in 1913, attributed the change in rate of migration of colloidal arsenic sulfide under the influence of light to a direct effect on the static charge carried by the suspended particles, primarily a photoelectric effect.

After the report of Winther (IV-155) on the photovoltaic effect of zinc oxide, Burgin (IV-43) studied the effect with zinc oxide suspensions in water with and without cathodic depolarizers (dyes or metallic salts) or anodic depolarizers (glucose, glycerol, or benzidine), and with and without both. The formation of zinc peroxide was postulated to account for the alteration of the sign of the photopotentials in the dark (after exposure to light). Baur's theory (VI-6, 7, 8) of sensitized photolysis was supported.

Hoja (IV-81) found that an aqueous suspension of pure zinc oxide freed from adsorbed water did not show a photovoltaic effect (in contrast to the results of Burgin (IV-43)); the presence of a small amount of hydrated zinc oxide produced the effect. If it is assumed that the hydrated compound acts as a cathodic depolarizer, the results agree with the theory of Baur (VI-8). Hoja (IV-82) found that the photoelectric sensitivity of a platinum electrode in an aqueous zinc oxide suspension depended on the liquid phase and also on the previous history of the platinum.

Summary on photovoltaic cells of Type IV

Results of investigations in this field seem to indicate that the thermal potential is small and often of the opposite sign to that of the over-all potential. The results are inconclusive, but the primary effect seems to be the photochemical alteration of the electrode coating which may result in a positive or negative effect, depending upon the nature of the electrolyte ions present.

IX. PHOTOVOLTAIC CELLS OF TYPE V: METAL ELECTRODES COATED WITH A DYE AND IMMERSED IN SOLUTIONS OF ELECTROLYTES

Moser (IV-104), in 1888, discovered that the photopotentials produced by sunlight on electrodes of silver chloride, bromide, or iodide was considerably increased by immersing the electrodes in a bath of a dye such as erythrosin. Rigollot (IV-115) studied undyed and dyed copper–cuprous oxide electrodes,

using eosin, erythrosin, safranine, malachite green, Crystal green, and Soluble blue.   He found a severalfold increase in the photocurrent for the dyed electrodes; the most effective light was that within the band of maximum absorption of the dye.

Stora (V-6 to 15) has made an extensive study of the photovoltaic effect produced by metal electrodes covered with many different dye films and immersed in aqueous solutions of inorganic salts.   She reported the following conclusions:

(1) The potential is independent of the metal (V-6).

(2) Most photopotentials are negative except for fluorescent dyes (V-8).

(3) Most photopotentials are due to a reduction for which the chromophore group is responsible (V-8).

(4) The auxochrome group has no effect (V-8).

(5) There is a positive effect in the neighborhood of the absorption bands, which is probably due to a shift in the oxidation–reduction equilibrium (V-6).

(6) The sensitivity curve is similar to the light-absorption curve of the absorbed dye but with a lag of 100-1500 Å., which increases with the concentration. This is interpreted as an indication that only the portion of the dye in immediate contact with the electrode is photosensitive and the rest of the dye molecule merely acts as an absorbent screen (V-7).

(7) There is a definite relation between the photopotential and the proportion of dye reduced in the dyed layer (V-9).

(8) A platinum electrode with an adsorbed photosensitive dye behaves toward a reducer as an inert electrode in an oxidation–reduction medium (V-9, 14).

(9) The negative photopotential of dyed platinum electrodes is diminished by bubbling oxygen through the solution, is inverted by nitrogen, and becomes strongly positive with hydrogen (V-10).

(10) Photoelectric effect and photochemical sensitiveness both result from oxidation and reduction dependent on the chemical constitution of the dye and on the nature of the solvent (V-12).   The Becquerel effect is the resultant of the positive effect due to the oxidizability of the reduced form and the negative effect to the reduceability of the oxidized form (V-14).

(11) The photopotentials of xanthane dyes are markedly reduced by hyposulfites, phenols, amines, and titanous chloride (V-11).

(12) The rules regarding the effect of pH on the photoeffect of electrodes coated with a metallic salt do not apply to dyed electrodes (V-13).

(13) For metal electrodes, such as copper, covered first with the oxide and then dyed, the potential of the metallic compound is superimposed on the potential due to the presence of the dye (V-6).

(14) An increase of temperature decreases the positive photovoltaic effect and increases the negative effect (V-15).

Schlivitch (V-5) reported that the electrodes in the cell

$$Cu \mid CuSO_4(aq.) \mid Cu$$
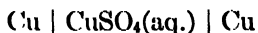
became sensitized because of the presence of a dye such as methylene blue, but he attributed the sensitivity to the oxidation of the copper which is effected more

rapidly in the presence of the dye. He reported that zinc electrodes are sensitized only to a very small extent by methylene blue.

Nga (V-3, 4) studied dyed platinum and copper electrodes and attributed the photovoltaic effect to a displacement of the oxidation–reduction equilibrium following photolysis of water. She found no effect on illuminating colored electrodes in glycerol containing dissolved potassium iodide of various concentrations, but the effect appeared upon the addition of water.

Sheppard and coworkers (IV-134, 135) have studied dye-sensitized silver–silver halide electrodes. Their experiments indicated the release of photoconductance electrons, either by the adsorbed dye itself or by the halide ions receiving energy from the photoactivated dye. Light which was absorbed by the adsorbed dye, but not by the silver halide itself, produced relatively large photocurrents. The adsorbed dye acted also as a halogen acceptor, diminishing the positive effect.

Kameyama and Hukumoto (V-2) studied the photoconductance of dye-sensitized silver bromide and concluded that, in the region sensitized by the dye, the electron was set free or raised to the conduction band by the energy of light absorbed by the dye adsorbed on the silver bromide.

Summary on photovoltaic cells of Type V

Results of investigators seem to indicate that for metal electrodes coated with a dye the main effect is caused by photochemical alteration of the dye. This alteration may result in a shift of the oxidation reduction equilibrium or may actually emit an electron from the dye or from the sensitive layer. The sensitivity curve is similar to the light-absorption curve of the adsorbed dye, but is slightly modified by the thermal effect and by the effect of the metal electrode itself.

X. SUMMARY

The results of this study have presented a number of ideas with reference to the mechanism involved in the production of photopotentials in the "wet"-type of photovoltaic cells. Among these are the "local-cell" theory of Tucker, the "increased-solubility" theory of Garrison, the "photolysis" theory of Audubert, the "photoelectric" theory of Goldmann and others, the "activated-molecule" theory of Dufford, the "ion-adsorption" theory of Fajans, and the "photochemical" theory of numerous investigators.

The work of Sheppard, Vanselow, and Trivelli reveals in an interesting manner a probable cause of both the negative (inertialess movement of an electron) and the positive (slower movement of an ion or an atom) responses which so often characterize the coated-electrode type of photovoltaic cells.

Several attempts have been made to account for the photovoltaic potentials more or less quantitatively. Baur (VI-6, 7, 8; III-1, 2) developed theoretical formulas covering photolyses in different conditions of inhibition, autocatalysis, etc., on the basis of his theory of photosensitization, in which the catalyzer is assumed to act as an oxidizing and reducing agent. Bancroft (VI-2 to 5) has

summarized the photophenomena in terms of the principles of the electrochemistry of light.   Russell (II-39) derived an equation for the variation of the photopotential with time, using the photochemical modification theory and the effect of diffusion on the potential developed.   Adler (VI-1) has applied Kimball's (VI-11) treatment of the theory of absolute reaction rates to the positive primary photopotential.   Magee and Eyring (VI-13) have also used the theory of absolute reaction rates to calculate the measured potential at an electrode displaced from equilibrium by a photochemical reaction; they have compared their results with experimental results for the photovoltaic effect.   Lange (VIII-4) presents evidence to prove that the observed photovoltaic effect is the same fundamental
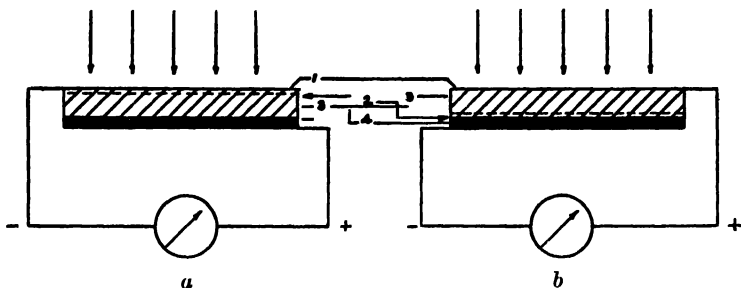
Fig. 4. Illustration of (a) front-wall and (b) back-wall cells.   1, translucent electrode; 2, insulating layer (barrier layer); 3, semiconductor; 4, supporting electrode.
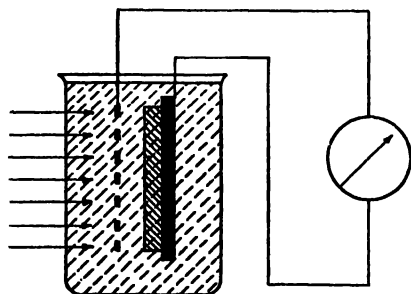
Fig. 5. Schematic diagram of a cell in which a liquid is present (Becquerel cell)

photoelectric process that is present in the crystal photoeffect and the barrier-layer photoeffect.   He groups these three phenomena together as "semiconductor photoeffects".   Lange's idea of the similarity in these three phenomena is illustrated by means of figures 4 and 5.   In figure 4 he illustrates the "front-wall" and "back-wall" cells; the difference depends upon the position of the insulating layer.   He calls attention to the fact that it is not essential that the front translucent electrode be a metal; it can also be a conducting liquid or an electrolyte. This leads him to a schematic diagram (figure 5) of a cell in which a liquid is present,—he names it an "electrolytic semiconductor photocell" (Becquerel cell).

An interesting sidelight is thrown onto this topic by Lifschitz (II-22), who

suggests that we refer to the "photovoltaic effect" only when it appears impossible to formulate the chemical reaction for a difference of potential caused by light. Baur (VI-8) suggests that the Becquerel effect is the symptom of a hidden photochemical change in a material system.

In general, the evidence to date seems to be sufficient to warrant the following conclusions: Certain cells seem to be very sensitive to small temperature variations; irradiation may produce sufficient heat effect to account for at least a part of the potential observed. For pure metals in inert electrolytes the photopotential may be primarily photoelectric, but these potentials are usually quite small. For metal electrodes in light-sensitive solutions the effect is primarily due to the photochemical alteration of the electrolyte. For coated electrodes the effect may be a combined photoelectric–photochemical process taking place in the coating material. The possibility of photolysis of water is not ruled out but requires more supporting evidence. It seems very likely that the observed photovoltaic effect is probably the resultant of several of these effects and that that effect which predominates depends upon the type of electrode-electrolyte system under investigation. Better data are now needed to identify and measure the separate effects.

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EXPERIMENTAL METHODS OF DETERMINING THE ACTIVATION ENERGIES OF ELEMENTARY REACTIONS[1]

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CONTENTS

I. Introduction

The present discussion will be limited to those elementary reactions which involve the participation of atoms and free radicals of short life, and which occur in the gas phase. Such elementary reactions are very frequently assumed as intermediate steps in the mechanism of thermal and photochemical processes. It is therefore of obvious importance to investigate their rates by independent means. Unfortunately, the short life of the substances involved makes ordinary methods of investigation impossible, and thus necessitates the use of rather indirect methods of attack. This arises from a number of causes: (a) It is impossible to prepare substances of such short life in high concentration, or in a state of purity. As a result the atoms or radicals must usually be prepared *in situ*, in the presence of a very large excess of other substances. (b) On account of the short life of the active substances, their estimation and identification are difficult. (c) The products of an elementary reaction often include other substances of short life. These substances react further, and it is often very difficult to disentangle the primary process from such secondary reactions. (d) The methods of preparing atoms and radicals often produce several active species simultaneously; hence numerous side reactions may occur which mask the process under investigation.

To make an unequivocal determination of the activation energy of an elementary reaction the following information is necessary: (a) what atoms or radicals are produced by the method employed; (b) the concentrations of the atoms or radicals and of other substances; (c) the amount of product produced in a definite time, and the identity of the product; (d) the effect of temperature on (a), (b), and (c); (e) the occurrence of secondary or side reactions, and their rates, temperature dependence, etc.

There is no question that up to the present no investigation of an elementary reaction has yielded direct and accurate information on all the above points. As a result, information on the activation energies of elementary reactions comes from a knowledge of one or more of the above factors, together with inference from analogous cases, etc., in place of the deficient information. The results are therefore, as Kassel puts it, "tainted with contingency." However, as information accumulates, more and more confidence can be placed in the values assigned to the simpler reactions, and reliable information is steadily forthcoming.

It may be pointed out (cf. Rice (242)) that we are primarily interested in the activation energies of four main types of process: (1) the rupture of a bond in a stable molecule, leading to the formation of atoms or radicals; (2) reactions between atoms or radicals and molecules; (3) reactions between two atoms or radicals; and (4) the decomposition of radicals.

Virtually all the estimates of activation energies have been made by one of the following procedures:

(a) *The rate of production of the product is measured as a function of temperature.* For example, the photolysis of mercury dimethyl leads to the production of

methyl radicals. In the presence of butane, methane is formed. This is assumed (278) to be due to the occurrence of the reaction

$$CH_3 + C_4H_{10} = CH_4 + C_4H_9$$
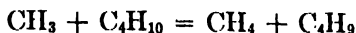
By measuring the rate of formation of methane as a function of temperature, we can thus arrive at the activation energy of this reaction.[2]

(b) *The rate of disappearance of the reactant is measured as a function of temperature.* Thus the reaction

$$H + C_3H_8 = C_3H_7 + H_2$$
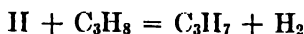
is followed by determining the rate of disappearance of propane in a system containing propane and hydrogen atoms (292).

(c) *The value of the activation energy is obtained by an analysis of the mechanism of a complex change.* Thus we may make an approximate estimate of the activation energy of the reaction

$$H + C_2H_5 = 2CH_3$$

from an analysis of the mechanisms of various reactions involving ethane and hydrogen atoms (295, 296, 324).

(d) *The activation energy is obtained from the rate of reaction at one temperature, together with suitable assumptions about the frequency factor.* This method is very frequently employed.

(e) *The lower or upper limit to the value of the activation energy is obtained by the appearance or non-appearance of the reaction under certain conditions.* Thus hydrogen atoms do not react with methane at room temperature in a contact time of 1 sec., so that it may be concluded that the activation energy is not less than 10 kcal. (98). In such cases there is always the danger that the non-occurrence of the reaction is due to a low frequency factor, rather than to a high activation energy.

(f) *The relative values of the activation energies of two reactions may be inferred by assuming equal frequency factors (or by assigning different values to them on the basis of steric or other considerations) and comparing the amounts of products formed.* Thus in the photolysis of methyl ethyl ketone equal amounts of methyl and ethyl radicals are presumably formed. Since the amounts of ethane, propane, and butane obtained as products are roughly those estimated from

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[2] In this, and in practically all other cases, the activation energy is calculated from the Arrhenius equation

$$\kappa = Ae^{-E/RT}$$

assuming A to be temperature independent. While this is not strictly true, it introduces no appreciable error with the accuracy attainable. In other words, for the present purpose we may assume the Arrhenius equation to be an experimental fact.

probability considerations (174), it may be concluded that there is little difference in the activation energies of the three recombination reactions

$$2CH_3 = C_2H_6$$

$$2C_2H_5 = C_4H_{10}$$

$$CH_3 + C_2H_5 = C_3H_8$$
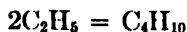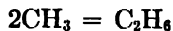
(g) *The activation energies of part reactions are obtained by comparing an assumed mechanism with experiment.* This method has been widely used by Rice (212).

(h) *The result is obtained by inference from thermal data and bond strengths.*

(i) *The result is obtained from a knowledge of the activation energy of the reverse reaction, and of the heat of reaction.* In practice the main difficulty here is that we rarely know the heats of elementary reactions with any degree of accuracy.

(j) *Theoretical methods.* These are beyond the scope of the present review.

II. EXPERIMENTAL METHODS

In general, the two characteristic features of any experimental method are (A) the means of producing the active species, and (B) the method by which they are estimated. In the following pages we shall discuss these two questions in detail separately, together with a description of the main combinations of the two which have been used in practice. Ordinary methods which are used for the investigation of reactions of stable substances will not be discussed here.

A. THE METHODS OF PRODUCING ATOMS AND RADICALS

1. Thermal

(a) Active species in thermal equilibrium with the substance from which they are produced

In the case of the common diatomic molecules, sufficient information exists to enable the degree of dissociation to be calculated precisely at all temperatures. Table 1 gives the temperatures corresponding to various amounts of dissociation when the pressure of the gas is 1 mm. (91). It will be seen from the table that at room temperature the alkali metals are appreciably dissociated into atoms; at moderate temperatures iodine is as well. With most other diatomic molecules, however, very high temperatures must be reached before the atom concentration becomes appreciable.

Definite information about the dissociation of more complex molecules has been obtained experimentally in a few cases. For example, Bonhoeffer and Reichardt (37) made a spectroscopic investigation of the dissociation of water vapor, and determined the equilibrium for the reaction

$$H_2O \rightleftharpoons H + OH$$

In general, this method is of little use in the production of free radicals by the thermal decomposition of organic molecules. The strengths of the bonds in

organic molecules are still a matter of controversy. The values given by a number of workers are listed in table 2, and a very consistent and plausible set recently given by Baughan, Evans, and Polanyi is shown in table 3. It is evident that, whatever the true values may be, they are so high that, except possibly in the case of the iodides, the equilibrium concentration of free radicals or atoms is far too small to be of importance except at temperatures so high that secondary reactions come into play and make the situation extremely complex. As a result, little use can be made of the stationary-state concentration of free radicals in equilibrium with organic molecules, and the method has not been widely used, except in a few special cases. The main examples of

TABLE 1

Dissociation of diatomic molecules (from Geib (91))

Pressure = 1 mm.

SUBSTANCE	HEAT OF DISSOCIATION	TEMPERATURE AT WHICH THE DEGREE OF DISSOCIATION IS		
		1 per cent	0 01 per cent	0 0001 per cent
	kcal.	°K.	°K.	°K.
K_2	11.8	270		
Na_2	17.0	390	280	
Li_2	26.7	590	420	330
I_2	35.2	680	510	410
Br_2	45.2	850	640	510
Cl_2	56.9	1040	800	640
HI	70	1310	975	780
HBr	86.7	1590	1200	965
HCl	101.5	1830	1380	1115
H_2	102.7	1910	1425	1140
D_2	104.6	1920	1440	1160
S_2	102.6	1930	1430	1140
O_2	117.4	2000	1530	1240
P_2	115	2200	1620	1260
NO	122.5	2100	1600	1290
CO	160 (?)	2580	1990	1620
N_2	170	2850	2200	1800

its use in connection with the investigation of elementary reactions are: (*1*) reactions involving atomic hydrogen; (*2*) reactions involving atomic sodium; (*3*) reactions involving potassium, magnesium, cadmium and zinc atoms; and (*4*) reactions involving iodine atoms.

(*1*) *Reactions involving atomic hydrogen:* The thermal conversion of para- to ortho-hydrogen was investigated by Farkas (69, 70) at temperatures in the range 600° to 750°C. The reaction was of the 3/2 order, indicating the mechanism

$$H_2 \rightleftarrows 2H$$

$$H + p\text{-}H_2 = o\text{-}H_2 + H$$
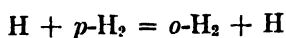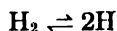
TABLE 2
The strength of bonds in organic molecules (from Rollefson and Burton (254))

BOND	STRENGTH	REFERENCE
	kcal.	
C—C............	82.5 (hydrocarbons)	(242)
	83	(204)
	84.2 (paraffins)	(205)
	110–115	(169, 170)
	71	(68)
	97.6	(324)
	72.1 (ethane)	(41)
	89.5 (ethane)	(179)
C=C..	162 (ethylene)	(179)
	145 (hydrocarbons)	(242)
	149	(204)
	200	(169, 170)
	125	(68)
	151.2 (olefins and cyclic compounds)	(205)
C≡C....	198.5 (acetylenic hydrocarbons)	(205)
	220.5 (acetylene)	(179)
	200	(204, 242)
	187	(218, 219)
C—H...............	100 (hydrocarbons)	(242)
	92.3	(176)
	94.8 (methane)	(41)
	100 (methane)	(205)
	92	(68)
	114	(169, 170)
	102.5	(199, 200)
	108	(324)
	103 (methane)	(179)
C—O	92	(68)
	82 (alcohols, ethers)	(242)
	81.8	(204)
	83 (aliphatic ethers)	(205)
	81 (aliphatic primary alcohols)	(205)
C=O	178 (formaldehyde)	(179)
	183.5 (acetone)	(179)
	188	(68)
	177.8 (ketones)	(205)
	166.1 (formaldehyde)	(205)
	174.4 (other aldehydes)	(205)
C—Cl...............	78 (alkyl halides)	(242)
	73	(68)
	71	(99)
C—Br...............	65.3	(204)
	58	(99)

TABLE 2—*Concluded*

BOND	STRENGTH	REFERENCE
	kcal.	
C—I	56.5	(204)
	41	(68)
C—N	64.2 (methylamine)	(179)
	66 (amines)	(242)
	68.4 (amines)	(205)
C≡N	200 (nitriles, HCN)	(242)
	202 (HCN)	(205)
	209.2 (aliphatic cyanides)	(205)
	207.5 (HCN)	(179)

TABLE 3

Estimates of bond strengths by Baughan, Evans, and Polanyi (15a)

R	BOND STRENGTHS			
	R—H	R—I	R—CH₃	R—OH
	kcal.	*kcal.*	*kcal.*	*kcal.*
CH₃	103.6	55.0	88.2	87.6
C₂H₆	96.1	51.2	83.1	86.2
n-C₃H₇	95.5	50.7	82.8	86.7
iso-C₃H₇	91.0	48.4	80.2	86.5
tert-C₄H₉	86.9	46.3	76.9	87.6

In a similar way, Farkas and Farkas (73) investigated the thermal conversion of ortho- to para-deuterium, and the reactions

$$H + D_2 = HD + D$$

and

$$D + H_2 = HD + H$$
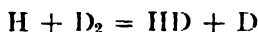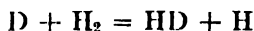
There seems to be no doubt that in all these cases the reaction proceeds through the agency of the stationary concentration of hydrogen or deuterium atoms in thermal equilibrium with undissociated molecules.

The thermal reactions of deuterium with methane, ammonia, and water also appear to proceed through the agency of the equilibrium concentration of deuterium atoms (72, 75). However, it is only with exceptionally stable substances, such as ammonia, methane, and water, that this method can be used to investigate the hydrogen-atom reactions, since with most substances the high temperatures necessary would result in decomposition and other complications.

(2) *Reactions involving atomic sodium:* As we have seen, sodium, even at room temperature, is appreciably dissociated, and at 200° to 300°C. it is mainly

in the atomic state. The reactions of sodium with many substances have been investigated by Polanyi and his coworkers by two rather similar methods. The so-called method of dilute flames is a modification of the flow method (see section (b) (1) on page 236) which is suitable for the investigation of very fast atomic reactions.

The original form of the method, that of "highly dilute flames," is as follows (20, 21, 22, 27, 214): Two reactants, A and B, are led into a tube from opposite ends. The pressures are so low that the mean free paths are greater than the diameter of the tube. Under these circumstances the gases mix solely by diffusion. As A penetrates into B it is consumed, and its pressure sinks to zero. Similarly with B, as it penetrates into A. We thus have the state of affairs shown in figure 1. The curve U represents the product $P_A P_B$, and should thus be proportional to the rate of reaction if the reaction is bimolecular. The essential feature of the method is the determination of the rate of reaction from the
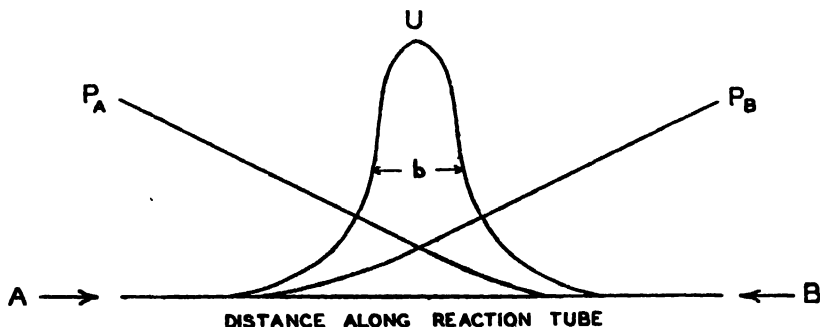
Fig. 1. The method of highly dilute flames. Curve showing consumption of reactants and formation of product as a function of distance along the reaction tube.

breadth of the curve. It is obvious that a relationship should exist, since the slower the reaction the farther the reactants will penetrate into one another. The exact relation is

$$k = \frac{27}{b^3} \frac{1}{2qUk_A k_B}$$

where k is the rate constant of the reaction, k_A and k_B are the diffusion resistances of the two gases, q is the cross section of the tube, and b is the "half-breadth" of the curve U. The form of the curve is easily obtained if the product of the reaction is a solid. Thus in the reaction between sodium and chlorine, the curve can be obtained from the thickness of the sodium chloride deposit at any point. This can be obtained by direct weighing or by opacity measurements.

By a determination of the over-all rate constant in this way, together with an examination of the luminescence accompanying the reaction, Polanyi and his collaborators have obtained information about the rates of many reactions

involving metal atoms, and incidentally about reactions of halogen atoms, etc.; e.g., the reactions

$$Na + Cl_2 = NaCl + Cl$$

$$Cl + Na_2 = NaCl + Na$$

$$Na + Cl = NaCl \text{ (on wall)}$$
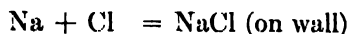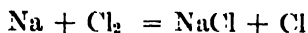
For a review of this work see Polanyi (214).

A modification of this method is that of "diffusion flames." This is suitable for reactions somewhat slower than those considered above, i.e., for those with an activation energy of a few kilocalories (118, 119, 120, 123, 171). This method is similar to the dilute-flame method, in that the rate of reaction is inferred from measurements of the distance which one component penetrates into the other before being used up. To make this distance shorter so that slow reactions can be investigated, a foreign gas at a pressure up to 10 mm. is added. This slows
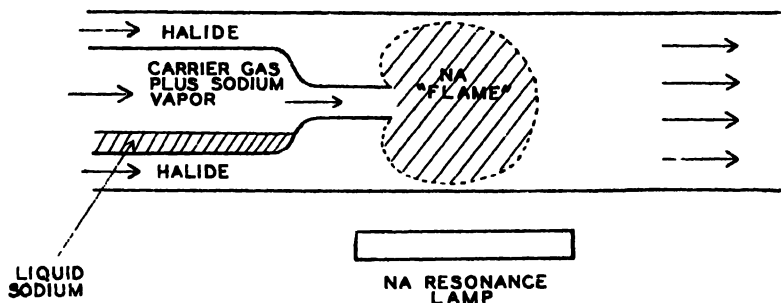
Fig 2. The method of diffusion flames

down diffusion and acts as a carrier for the reactants. The apparatus is illustrated in figure 2.

One reactant, say sodium vapor, together with an inert gas as carrier enters through a jet into a chamber containing the other reactant, say methyl chloride. The partial pressures of the reactants are of the order of 2×10^{-3} mm. for sodium, and 0.02 to 0.5 mm. for the alkyl halide. By illuminating the sodium vapor with a resonance lamp giving the D doublet, it is possible to make the sodium vapor visible. We can thus measure the size of the "flame" to a distance at which the concentration of sodium vapor is so low that it cannot be detected by this method. We can then calculate the rate constant of the reaction from the size of the flame, or zone of penetration of one reactant into the other, by means of considerations similar to those used in the case of the dilute-flame method.

Experimentally the conditions are adjusted so that for simplicity (1) the size of the flame is smaller than the tube diameter, and wall effects are thus eliminated, (2) the rate of flow of carrier gas in the jet is fast enough so that no appreciable back-diffusion of the reactant against the sodium stream occurs, and

(*3*) the flow of the reactant and its amount are so arranged that its concentration is constant throughout the tube, and is not appreciably affected by the flow of carrier gas, or by reaction. (It is always present in large excess compared with sodium.)

In practice, the partial pressure of the reactant is varied until a certain size of flame is produced. It is evident that the slower the reaction rate, the higher will be the necessary partial pressure. Thus with methyl iodide, where reaction occurs at approximately every collision, 10^{-3} mm. is sufficient, while with methyl fluoride even with a pressure of 10 mm. the reaction is so slow that the whole tube is full of sodium vapor, i.e., less than one collision in 10^{6} is effective. In general, the suitable range of reactions the rates of which can be measured are those in which from 1/10 to 1/100,000 of the collisions between the reactants are effective.

Polanyi and his coworkers have investigated a whole series of reactions by this method, all of them involving metal atoms and halides: e.g.,

$$Na + CH_3Cl = NaCl + CH_3, \text{ etc.}$$

The absence of luminescence from the reactions results in it not being possible to obtain as much information about secondary reactions as is the case with the dilute-flame method. It has, however, proved possible to make accurate measurements of the activation energies of numerous metal atom–halide reactions (214).

(*3*) *Reactions involving potassium, magnesium, cadmium, and zinc atoms:* The situation here is the same as that for sodium (214).

(*4*) *Reactions involving iodine atoms:* The thermal decomposition of ethylene iodide is strongly catalyzed by iodine, and the rate is proportional to the square root of the iodine concentration (8, 216, 263). There seems to be no doubt that we have the reactions

$$I_2 \rightleftarrows 2I$$

$$I + C_2H_4I_2 = I_2 + C_2H_4I, \text{ etc.}$$
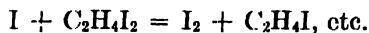
It is known that I_2 catalyzes a large number of decompositions, possibly through the intermediate formation and decomposition of an alkyl iodide. (See reference 262 for a review of catalysis by iodine.)

(b) Production of active species by thermal decomposition

Atoms or radicals are produced in the thermal decomposition of many substances. The methods by which advantage is taken of this fact in practice are numerous, and differ mainly in the time during which the reactant remains in the heated zone.

(*1*) *The static and flow methods:* Using the ordinary static and flow methods, atom or radical reactions can be investigated by mixing a substance, the sensitizer, with the reactant and heating the mixture to a temperature at which the reactant is normally stable, while the sensitizer decomposes with the formation of atoms or radicals. The first investigation of a sensitized reaction of this kind

was that of Taylor and Jones (312), who investigated the decomposition of mercury and lead alkyls in the presence of hydrogen and ethylene. They found that the main result was polymerization of the ethylene, pointing to the occurrence of the following reactions:

$$Hg(CH_3)_2 = Hg + 2CH_3$$

$$CH_3 + C_2H_4 = C_3H_7, \text{ etc.}$$
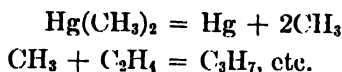
In order to apply the method in such a way as to obtain quantitative information, it is essential to know the kinetics of the decomposition of the sensitizer, and especially the radicals formed in its decomposition. As a result, the sensitizers which have been at all widely used are comparatively few in number. The main ones are ethylene oxide, azomethane, acetone, and metal alkyls.

The decomposition of *ethylene oxide* was first investigated by Heckert and Mack (121) in the temperature range 380° to 444°C. They showed that the reaction was of the first order, the rate at high pressures being given by

$$k_\infty = 6.3 \times 10^{11} e^{-52000/RT} \text{ sec.}^{-1}$$

The products were approximately 50 per cent carbon monoxide, 36 per cent methane, 7 per cent ethane, and 7 per cent hydrogen.

The mechanism of the reaction was discussed by Sickman (269). He concluded that the complexities of the reaction could be explained on the assumption that the mechanism is as follows:

(1) $\qquad\qquad (CH_2)_2O = 2R$

(2) $\qquad\qquad (CH_2)_2O = CH_3CHO$

(3) $\qquad R + CH_3CHO = RH + CH_3CO = RH + CH_3 + CO$

(4) $\qquad\qquad 2R + M = X + M$
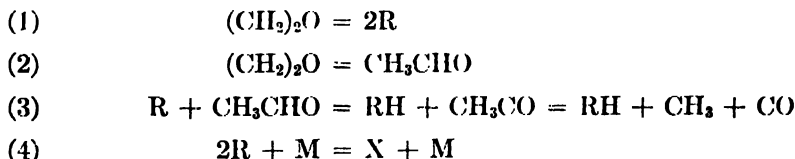
where R represents a free radical, X a molecule, and M is any third body. All the experimental facts are readily interpreted on this basis if we assume that k_1 is much smaller than k_2, i.e., that most ethylene oxide molecules isomerize to acetaldehyde, which then undergoes a radical-sensitized decomposition, and that relatively few ethylene oxide molecules give free radicals by reaction 1. It should be noted that the sensitized decomposition of acetaldehyde will not affect the radical concentration, since each radical removed by reaction 3 is regenerated.

Fletcher and Rollefson (79, 81) reinvestigated the reaction with special emphasis on the rôle of free radicals. Their work led them to postulate a mechanism of the type suggested by Sickman, but of a more detailed nature:

(1) $\qquad\qquad (CH_2)_2O = HCHO + CH_2$

(2) $\qquad\qquad (CH_2)_2O = CH_3CHO$

(3) $\qquad CH_2 + (CH_2)_2O = 2CH_3 + CO$

(4) $\qquad CH_3 + CH_3CHO = CH_3 + CH_4 + CO$

(5) $\qquad\qquad 2CH_3 = C_2H_6$
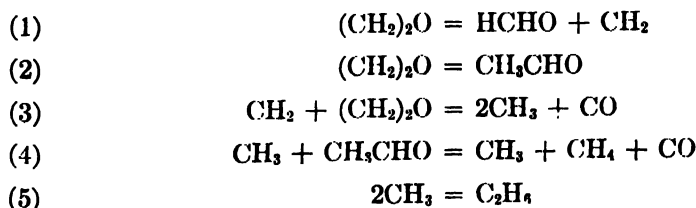
This mechanism is in good agreement with their rate measurements, analyses for formaldehyde and acetaldehyde, etc. By assuming that all the hydrogen found in the products comes from the decomposition of formaldehyde formed by reaction 1, and that all the ethane comes from reaction 5, they calculate that 14 per cent of the ethylene oxide decomposes by reaction 1. Whence, since each methylene gives rise to two methyls, they calculate that 0.3 methyl is formed for each ethylene oxide molecule decomposed.

While it cannot be said that this mechanism is established, it is undoubtedly plausible, and all the evidence indicates that by no means all the ethylene oxide decomposes by way of free radicals. It seems very unlikely that Fletcher and Rollefson's estimate of the fraction of ethylene oxide molecules giving rise to radicals is too low, although it may well be too high, since hydrogen and ethane may arise in other ways.

Many investigations have been made using ethylene oxide as a sensitizer (58, 79, 80, 81, 121, 287). The production of carbon monoxide has usually been used as an indication of the amount of decomposition of ethylene oxide, and hence of the number of methyl radicals generated in the system. It should, however, be noted that there is a possibility, especially when ethylene oxide is present in small quantity, that reactions involving methylene may be important.

Thus, Echols and Pease (58) investigated the ethylene oxide-sensitized decomposition of a number of paraffins by mixing the paraffin and ethylene oxide at temperatures around 400°C., allowing the ethylene oxide to decompose, and then analyzing the products for unsaturates and carbon monoxide. On the assumption that all the unsaturates come from the paraffin and all the carbon monoxide from the ethylene oxide decomposition, the ratio C_nH_{2n}/CO is a measure of the chain length of the sensitized decomposition. Thus at 425°C. with an 8:1 mixture of n-butane and ethylene oxide, they found

$$C_nH_{2n}/CO = 12.0$$

Hence, if we assume 0.3 methyl is formed for each molecule of decomposing ethylene oxide, we obtain a chain length of about forty. It may be noted that, irrespective of any uncertainty about the mechanism of the ethylene oxide decomposition, these results definitely indicate that chains are set up, since even with the extreme, and unlikely, assumption of two radicals from each molecule of ethylene oxide decomposed, the chain length would still be at least six.

Much work has been done on the reaction involving *azomethane*, so that here we shall merely outline the main findings. (For an extended discussion see Schumacher (262).) The main over-all reaction in the azomethane decomposition is (224)

$$CH_3NNCH_3 = C_2H_6 + N_2$$
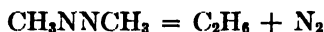
Small amounts of other products are also formed. The reaction is a classical example of a unimolecular change, the limiting high-pressure rate constants being given by

$$k_\infty = 3.13 \times 10^{16} e^{-52500/RT} \text{ sec.}^{-1} \quad \text{(Ramsperger)}$$
$$= 8 \times 10^{15} e^{-50200/RT} \text{ sec.}^{-1} \quad \text{(Rice and Sickman (249, 271, 272))}$$

It has been shown in a number of cases, examples of which are given later, that decomposing azomethane can induce the decomposition of other substances. This suggests that the decomposition process proceeds by way of free radicals, i.e.,

$$CH_3NNCH_3 = N_2 + 2CH_3$$
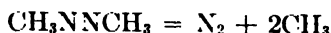
Experimental proof that at least part of the decomposition proceeds in this manner comes from the work of Leermakers (154) and of Rice and Evering (231), who showed that mirrors were removed when azomethane was decomposed by the usual Paneth–Rice technique. The evidence favors the idea that while azomethane decomposes by a free-radical mechanism, it does not do so by a chain mechanism (see 82, 122, 155, 227). Thus Leermakers found that at 275°C. ethyl radicals did not react with azomethane. Also, up to 260°C. the quantum yield of the photodecomposition is approximately 2; hence no long chains are set up by the methyl radicals produced in the primary process.

Taylor and Jahn (308) have recently reinvestigated the decomposition with emphasis on the analytical aspects of the problem. They conclude that the mechanism is

$$CH_3NNCH_3 = N_2 + 2CH_3$$

$$CH_3NNCH_3 + 2CH_3 = (CH_3)_2NN(CH_3)_2$$
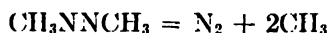
the ethane arising by secondary reactions. They find

$$k_\infty = 3.51 \times 10^{16}\, e^{-52500/RT}\ \text{sec.}^{-1}$$

in good agreement with previous work. On the basis of their mechanism, the rate of decomposition of azomethane into methyl radicals will be only half this.

There are numerous cases of decompositions induced by radicals from azomethane. Examples are the following: the decomposition of butane, and the polymerization of acetylene, of ethylene, and of propylene (Rice and Sickman (272)); the decomposition of acetaldehyde (Allen and Sickman (3, 270)); the decomposition of divinyl ether (Taylor (307)); the decomposition of heptane (Macss (167)); the decomposition of methyl ethyl ether and of propylamine (Rice, Walters, and Ruoff (247)).

The *acetone* decomposition has been the subject of many investigations, and the general kinetics appear to be fairly well established (128, 131, 246, 335). There is considerable evidence which indicates that methyl radicals are formed in the decomposition (1a, 156, 200, 201, 236, 244). Leermakers (156) has used the acetone decomposition to induce the decomposition of dimethyl ether.

Methyl alkyls are by far the most important sensitizers. There seems to be little doubt that in all cases the mechanism of the decomposition is

$$MR_x = M + xR$$
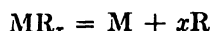
where M is a metal and R is an alkyl radical. The above process presumably occurs in steps:

$$MR_x = MR_{x-1} + R$$

$$MR_{x-1} = MR_{x-2} + R, \text{ etc.}$$

In interpreting the results of induced decompositions there are possible complications. For example, in the case of mercury diethyl, apart from the obvious secondary reactions,

$$2C_2H_5 = C_4H_{10}$$

and

$$2C_2H_5 = C_2H_4 + C_2H_6$$
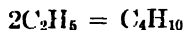
there is also the chance of

$$C_2H_5 + Hg(C_2H_5)_2 = C_2H_6 + HgC_2H_5 \cdot C_2H_4$$

or

$$C_2H_5 + Hg(C_2H_5)_2 = C_2H_6 + C_4H_{10} + Hg$$
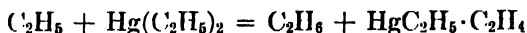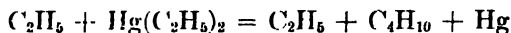
etc.

In general, however, there is no doubt that the main process is the simple formation of radicals, which then undergo secondary reactions. These substances have been used, for the most part, in two distinctly different ways for the investigation of radical reactions. In the one method a static system is used: the metal alkyl is decomposed in the presence of another substance and causes its induced decomposition. In the other method a flow system is employed: the metal alkyl is decomposed, and from the products obtained it is possible to draw conclusions regarding the relative rates of recombination and disproportionation reactions; viz.,

$$Hg(C_2H_5)_2 = Hg + 2C_2H_5$$

$$2C_2H_5 = C_4H_{10}$$

$$2C_2H_5 = C_2H_4 + C_2H_6$$
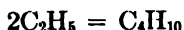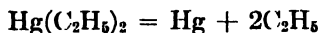
Information exists on the pyrolysis and photolysis of a large number of metal alkyls, and on their use as sensitizers, as indicated in table 4.

Various *other substances* have been used as sensitizers. Some examples follow: methyl ether (80); biacetyl (246a); ethyl ether (80, 82a); ethyl vinyl ether (325b); propane (127); butane (127); triphenylmethylazobenzene (261, 261a); silane (61); ethyl iodide (255a, 306a); ethyl bromide (255a); oxygen (158, 159, 160, 161, 162); products of paraffin decompositions (127); and tetraphenylsuccinic acid dinitrile (261a).

(2) The Paneth–Rice method—very fast flow: The method by which Paneth and Hofeditz (192) first discovered the free methyl radical is, in reality, only a very fast flow method. Since the main feature of this work is not the means by which radicals are produced, but rather the means used for their detection, the method is discussed in section B1 (page 255).

(3) Methods using heated filaments: The classical experiments of Langmuir were the first examples of this method (84, 150, 151, 152). Langmuir investigated the heat loss from metal filaments heated *in vacuo* or in the presence of hydrogen, oxygen, or other gases. The apparatus used was a more or less standard type of filament lamp bulb. He showed that at very high temperatures

hydrogen was dissociated into atoms on the filament, and that the atomic hydrogen thus produced reached the walls of the bulb at low pressures, where its activity was shown by the reduction of metallic oxides and by other reactions.

Considerable information on catalytic reactions has been obtained by this method, but in its ordinary form it is not of much assistance as far as homogeneous elementary reactions are concerned.

A modification of the method has been used by Storch (305). Storch wished to ascertain the initial products of the decomposition of methane, without complications due to secondary reactions. To accomplish this he decomposed methane at low pressures on a hot carbon filament in a "lamp-bulb" which was cooled in liquid nitrogen. The products thus condensed out immediately they

TABLE 4

Metal alkyls: pyrolysis, photolysis, and use as sensitizers

SUBSTANCE	REFERENCES		
	Pyrolysis	Photolysis	Use as sensitizer
Pb(CH$_3$)$_4$	(192, 275)	(157)	(15b)
Pb(C$_2$H$_5$)$_4$	(50, 155, 172, 195, 212)	(219a, 220, 320)	(51, 155, 156, 158, 274, 312)
Pb(C$_6$H$_5$)$_4$	(57, 196)	(157)	
Hg(CH$_3$)$_2$	(52)	(52, 61a, 165, 220, 278, 318, 320, 322)	(85, 244, 255, 278, 312, 318)
Hg(C$_2$H$_5$)$_2$	(312)	(174a)	(174a, 312)
Hg(C$_4$H$_9$)$_2$	(86, 196)		
Hg(C$_7$H$_{15}$)$_2$	(240)		
Si(CH$_3$)$_4$	(124)		
Si(C$_2$H$_5$)$_4$	(326)		
Si(C$_3$H$_7$)$_4$	(326)		
Ge(C$_2$H$_5$)$_4$	(90)		
Sn(C$_6$H$_5$)$_4$	(86)		
Bi(CH$_3$)$_3$	(192)		
Zn(CH$_3$)$_2$	(192)	(320)	
Sb(CH$_3$)$_3$	(192)		

were formed. He showed that under these circumstances the first recognizable product was ethane.

The main use of the filament method in the investigation of elementary reactions is that of Belchetz and Rideal (16, 17, 18). They employed two different types of apparatus. In both of these the gas streamed through at a high velocity (ca. 100 cm. per second) and at 0.1 mm. pressure over a heated platinum or carbon filament. In the first apparatus any radicals formed by the decomposition of the gas on the hot filament were caught on a water-cooled target 3 mm. away from the filament. Mirrors could be deposited on this target, and any products formed were caught in a liquid-air trap. Since the distance between the filament and the target was so small, of the order of one mean free path, any radicals formed would reach the target without undergoing

collisions. We should thus definitely be able to detect the radicals without any possibility of secondary processes intervening.

In the second apparatus the mirror was on the wall of the reaction vessel opposite the filament. It was considerably farther from the filament than in the former case, and the system thus resembled the hot-tube type of apparatus employed by Paneth and by Rice.

With both sets of apparatus tellurium and iodine mirrors were used, and platinum and carbon filaments. Most of the work was done with carbon filaments.

We shall return to this method later in connection with the detection of radicals. It may be mentioned here, however, that there is a considerable possibility that complications are introduced by the presence of the carbon, and that the activation energies of the decomposition of substances into free radicals calculated from the results may refer to catalytic processes on the surface of carbon or platinum, rather than to the homogeneous split into radicals in the gas phase. Certainly in Langmuir's work the dissociation of hydrogen into atoms occurred in an adsorbed layer of the surface of tungsten, and not merely by the molecule acquiring energy on impact. By analogy there seems every reason to suspect that, for example, a hydrocarbon may be adsorbed on the carbon filament prior to dissociation into radicals. Indeed, theoretical considerations are overwhelmingly in favor of such an occurrence. Evidence that this is the case will be presented later in discussing the detection of radicals produced by the Belchetz–Rideal method.

For a discussion of the production of hydrogen atoms by heated tungsten filaments, see Roberts and Bryce (251).

Haber and Oppenheimer (109) have used hydrogen atoms, produced by a hot filament, in a flow system to start sensitized explosions in hydrogen–oxygen mixtures at temperatures as low as 300°C. (see also 77, 108, 110).

(c) Production of active species by reactions of higher order than the first

In addition to their production by thermal decomposition, radicals and atoms may arise as intermediate stages in thermal reactions of higher order. In some cases they result from the interaction of two or more relatively stable molecules, while in other cases one radical by reaction with a normal molecule may form a different radical.

(1) Diffusion flames: Horn, Polanyi, and Style (129, 130, 215) modified the diffusion-flame technique so as to investigate certain reactions of free radicals. A further jet was added to the apparatus, and the products of a reaction of the type

$$Na + R \cdot Hal. = NaHal. + R$$
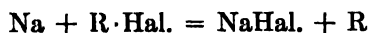
were introduced into chlorine or iodine. In this way they were able to demonstrate the occurrence of the reactions

$$R + Cl_2 = RCl + Cl$$

and

$$R + I_2 = RI + I$$
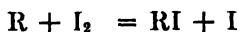
Allen and Bawn (2) have combined the method of Horn, Polanyi, and Style with the Paneth technique for the detection of radicals.

(2) *The indirect production of atoms and radicals:* Frequently the production of an atom or radical in a system leads, by reaction involving other substances, to the formation of other, different, atoms or radicals. For example, if mercury dimethyl is decomposed in the presence of propane (278), we have

$$Hg(CH_3)_2 = Hg + 2CH_3$$

$$CH_3 + C_3H_8 = C_3H_7 + CH_4$$
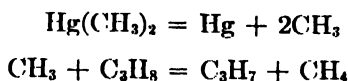
Hence this method could, in principle, be used as a source of propyl radicals. Other examples are

$$CH_3COCH_3 + h\nu = CO + 2CH_3$$

$$CH_3 + C_2H_4 = C_3H_7 \quad (314)$$

and

$$C_2H_6 + Hg(^3P_1) = C_2H_5 + H + Hg(^1S_0)$$

$$H + C_2H_5 = 2CH_3 \quad (106, 245, 296, 324)$$
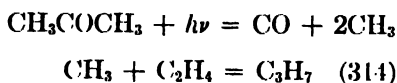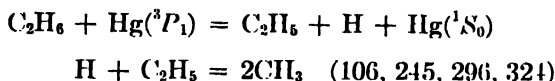
However, the systems thus formed are so complex that this is rarely a satisfactory method of generating atoms or radicals. Only when the complete mechanism of the reaction can be accurately established can this method be used.

(3) *Explosions, oxidation reactions, etc.:* There is considerable evidence that atoms and radicals play a decisive rôle in many explosions, oxidation reactions, etc. (134, 163, 180). The systems are so complex, and our knowledge of them is so slight, however, that they cannot be used in practice as reliable sources of atoms and radicals.

2. Photochemical

(a) Production of atoms or radicals by photolysis

A very wide variety of possibilities exist, since this section includes most of photochemistry. In many cases information about elementary reactions comes from an analysis of the mechanism of photolysis. A well-known example is the photosynthesis of hydrogen chloride, in which the primary process is the dissociation of chlorine, and the investigation of which leads to information about the secondary reactions

$$Cl + H_2 = HCl + H$$

and

$$H + Cl_2 = HCl + Cl$$
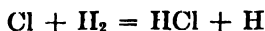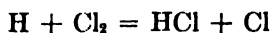
(For a recent and detailed discussion see Rollefson and Burton (254).) However, since it would obviously be out of place to enter into an extended discussion of photochemistry here, we shall consider only those cases in which a substance is deliberately photolyzed in order to provide a supply of radicals or atoms. Some of the main examples of this technique are:

(*1*) *Photohalogenations:* A wide variety of photohalogenations have been investigated (for reviews see references 181a, 254, and 262a). When a halogen absorbs light in the continuum the primary process involves a split into atoms, and if some other substance is present, the atoms thus produced may react with it. In general, chain reactions occur under these circumstances. In a large number of cases detailed investigations have been made, and the mechanism of the reactions can be inferred with considerable certainty. Activation energies of the part-reactions can then be deduced by a comparison of the rate equation predicted by the mechanism with that obtained experimentally. In this way activation energies have been arrived at for a large number of reactions involving atomic chlorine and bromine, and for a few reactions involving atomic iodine. Some examples follow:

$$Br + CHCl_3 = CCl_3 + HBr \tag{37a}$$

$$CH_3 + Cl_2 = CH_3Cl + Cl \tag{37b}$$

$$CCl_3CO + Cl_2 = CCl_4 + CO + Cl \tag{3b}$$
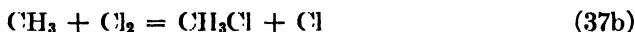
(*2*) *Photolysis of ketones:* The aliphatic ketones show a first absorption maximum in the neighbourhood of 2800 Å., which is associated with the carbonyl group. Much work has been done on the photolysis of a wide variety of ketones (see especially references 53, 105, 179, 181, 181a, and 279). It seems to be established that in the case of acetone the primary process is, at least to a large extent,

$$CH_3COCH_3^* = CH_3CO + CH_3$$
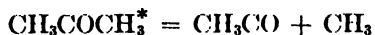
At higher temperatures (above 60°C.) the acetyl radical decomposes.

$$CH_3CO = CH_3 + CO$$
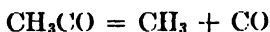
Hence at higher temperatures acetone acts as a source of methyl radicals only.

Pearson and his coworkers (100, 206, 208, 209, 210) have used mirror methods to detect and estimate free radicals in the case of acetone and numerous other ketones, and have used such photolyses as a source of free radicals. Estimates of the per cent of the primary step which involves decomposition into free radicals of various ketones are given in table 5.

Acetone has been used as a source of free radicals in the investigation of induced reactions by Leermakers (156), Taylor and Jungers (314), Maess (167), Akeroyd and Norrish (1), and Danby and Hinshelwood (53a).

(*3*) *Photolysis of metal alkyls:* The thermal decomposition of metal alkyls as a source of free radicals has already been discussed. The mechanism of their photolysis appears to be similar to that of their pyrolysis, yielding free alkyl radicals (52, 157, 165, 174, 181a, 220, 278, 318, 319, 320, 322). This may occur in stages; i.e., instead of

$$Hg(CH_3)_2 = Hg + 2CH_3$$

we may have

$$Hg(CH_3)_2 = HgCH_3 + CH_3$$

$$HgCH_3 = Hg + CH_3$$
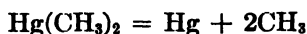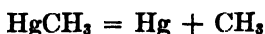
For a summary of work on the photolysis of metal alkyls see page 241.

The mercury alkyls have been much used as a source of free radicals by Taylor and his collaborators (52, 174, 278, 318), who by their use have investigated a whole series of reactions of the type

$$R_1 + R_2H = R_2 + R_1H$$
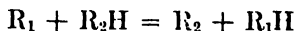
Thus, Smith and Taylor (278, 318) photolyzed mercury dimethyl in the presence of deuterium, ethane, neopentane, butane, isobutane, benzene, toluene, diphenyl-

TABLE 5

Estimates of the per cent decomposition into free radicals in the photolysis of several ketones (taken from reference 254)

KETONE	PER CENT DECOMPOSITION INTO FREE RADICALS	
	Glazebrook and Pearson	Norrish
Acetone.....	100	100
Methyl ethyl ketone..........	81	70–80
Methyl propyl ketone	62	
Methyl butyl ketone.	28	10
Dipropyl ketone.	37	37
Diisopropyl ketone.........	41	44

methane, and propylene. They assume in the case of the hydrocarbons that the main steps in the mechanism are as follows:

$$Hg(CH_3)_2 + h\nu = 2CH_3 + Hg \qquad I_{abs.}$$

$$CH_3 + RH = CH_4 + R \qquad k_1$$

$$R + CH_3 = RCH_3 \qquad k_2$$

$$CH_3 + CH_3 = C_2H_6 \qquad k_3$$
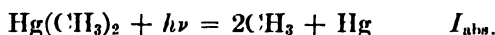
This yields for the rate of methane production

$$\frac{d}{dt}(CH_4) = k_1(RH) \cdot \frac{-2k_1(RH) + (4k_1(RH)^2 + 8k_3 I_{abs.})^{1/2}}{2k_3}$$

$$= k_1(RH) \cdot A$$

At low temperatures where ethane (from reaction 3) is the principal product, A will be approximately constant; hence the rate of production of methane will give a true measure of k_1. By measuring the rate of formation of methane as a function of temperature, the activation energy of reaction 1 can therefore be obtained. In this way they found, for example,

$$CH_3 + C_2H_6 = CH_4 + C_2H_5 \qquad E = 8.3 \text{ kcal.}$$

$$CH_3 + n\text{-}C_4H_{10} = CH_4 + C_4H_9 \qquad E = 5.5 \text{ kcal.}$$

$$CH_3 + C_6H_5CH_3 = CH_4 + C_6H_5CH_2 \qquad E = 5.6 \text{ kcal.}$$
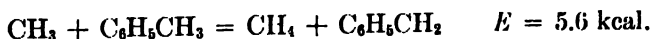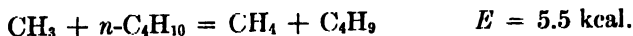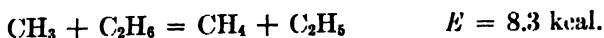
(4) Photolysis of alkyl halides: A great deal of work has been done on the absorption spectra and photolysis of the alkyl halides, especially the iodides (see, particularly, references 56, 62, 63, 64, 65, 181a, 329, 330, 331, and 332). There is some disagreement regarding the mechanism of the reactions, but the evidence is strongly in favor of a primary split into a radical and a halogen atom; e.g.,

$$RI + h\nu = R + I$$
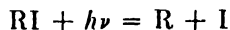
The quantum yield is low, owing to the high efficiency of the reverse reaction, but it may be increased by the addition to the system of any substance capable of fixing the iodine formed (133).

The photolysis of alkyl iodides has been used as a source of free radicals by Jungers and Yeddanapalli (137), using methyl, ethyl, propyl, and isopropyl iodides; by Tassel (306), using ethyl iodide; and by Joris and Jungers (133), using ethyl iodide.

(5) Photolysis of azomethane: A number of investigations of the photolysis of azomethane have been made (42, 43, 54, 82, 221, 225, etc.). Early work seemed to suggest a simple mechanism leading directly to the final products,

$$CH_3NNCH_3 + h\nu = C_2H_6 + N_2 \tag{1}$$
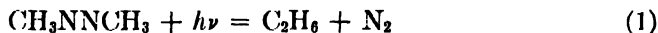
However, it now appears to be established that the primary step is a split into free radicals

$$CH_3NNCH_3 + h\nu = 2CH_3 + N_2$$

or

$$= CH_3 + NNCH_3$$
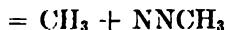
and that reaction 1 does not occur to any appreciable extent.

The photolysis of azomethane has been used as a source of free radicals by Maess (167) and by Blacet and Taurog (26a).

(B) PRODUCTION OF ATOMS OR RADICALS BY PHOTOSENSITIZATION

In order that a photochemical reaction may occur it is necessary (a) that the magnitude of the quantum of the incident light be large enough, and (b) that the light be absorbed. In many cases substances have dissociation energies corresponding to wave lengths in a convenient region of the spectrum, but are transparent down to the Schumann region where photochemical experiments are difficult to carry out. Thus, hydrogen has a dissociation energy of 102.7 kcal., corresponding to a wave length of 2776 Å., but the continuum in its absorption spectrum does not begin till 849 Å.

If we add to hydrogen a substance which will absorb somewhere below 2776 Å. and can transfer this energy to the hydrogen, we can produce a *photosensitized*

dissociation of hydrogen. This method is of wide applicability and a variety of sensitizers have been used for many reactions; e.g.,

$$Xe + h\nu(1469 \text{ Å.}) = Xe^*$$

$$Xe^* + H_2 = Xe + 2H \quad \text{(Calvert (45))}$$

and

$$NH_3 + h\nu = NH_3^*$$

$$NH_3^* + C_6H_{14} = C_6H_{13} + H + NH_3 \quad \text{(Farkas (76))}$$
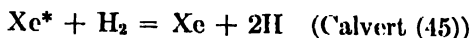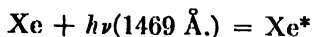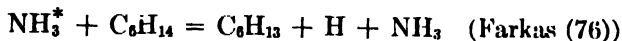
From an experimental point of view, however, the main sensitizers are metal atoms, since with them it is possible to use very intense and convenient sources of resonance radiation. Of these, mercury has been most used. In experiments of this sort mercury vapor is mixed with the reactant gas, and the mixture is illuminated with the mercury resonance line at 2537 Å. (A little work has also been done with the lower resonance line, 1849 Å. (48, 81a).) This is absorbed by the mercury vapor in the system, normal 6^1S_0 mercury atoms being raised to the 6^3P_1 level. This lies 4.8 volts, or 112 kcal., above the ground state. Such excited mercury atoms may then transfer their energy by collision to other molecules. If such transfer occurs efficiently a wide variety of reactions is possible, since 112 kcal. is greater than the activation energy of almost all chemical reactions (see, e.g., references 46, 309, 310, 311, and 316).

The mercury-photosensitization method is especially important, since Taylor and his coworkers have shown that it allows the investigation of reactions involving hydrogen atoms. In the presence of hydrogen and a reacting substance, X, we have

$$Hg(6^1S_0) + h\nu = Hg(6^3P_1) \tag{1}$$

$$Hg(6^3P_1) + H_2 = Hg(6^1S_0) + 2H \tag{2}$$

$$H + X = \text{Products} \tag{3}$$

$$2H + \text{(third body or wall)} = H_2 \tag{4}$$
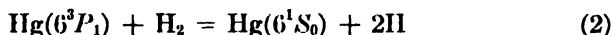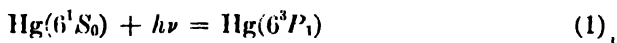
Under these circumstances a stationary concentration of hydrogen atoms exists, and, if the rates of reactions 1, 2, and 4 are known, the rate constant of reaction 3 can be calculated (see, for example, references 4, 5, 6, 7, 78, 277, 301 and 302). This is an extremely useful method, although the results are not always easy to interpret, since in many cases the reactant also "quenches" the resonance radiation to an appreciable extent, and decomposition reactions, and so on, are thus superimposed on the hydrogen-atom reaction. Examples

---

[*] From recent work there is some doubt as to whether reaction 2 proceeds as written, or goes by the following reaction (23, 89, 187, 250)

$$Hg(6^3P_1) + H_2 = HgH + H$$

followed by

$$HgH = Hg + H$$
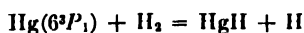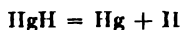
However, this would not affect the general conclusions to be drawn from experiments on photosensitization by mercury.

of the use of this method to investigate hydrogen-atom reactions are given below:

REACTION	INVESTIGATORS
II + CH$_4$	Taylor, Morikawa, and Benedict (175, 317) Steacie and Phillips (293) Farkas and Melville (75)
II + C$_2$H$_6$	Taylor and Hill (310, 311) Kemula, Mrazek, and Tolloczko (138) Steacie and Phillips (296)
H + C$_3$H$_8$	Taylor and Hill (310, 311) Steacie and Dewar (286)
H + C$_2$H$_4$	Taylor and Marshall (316) Taylor and Hill (310, 311) Melville (173) Jungers and Taylor (136)

By mercury photosensitization it is also possible to produce atoms and radicals by decomposition reactions, especially by reactions of the type

$$XH + Hg(6^3P_1) = X + H + Hg(6^1S_0)$$
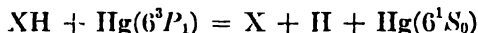
This has been much used, although it is generally difficult to make a sufficiently detailed interpretation of the mechanism to enable reliable estimates to be made of the activation energies of the individual elementary reactions. Examples are:

$$Hg(6^3P_1) + C_2H_6 = Hg(6^1S_0) + C_2H_5 + H \quad \text{(Steacie and Phillips (296))}$$

$$Hg(6^3P_1) + AsH_3 = Hg(6^1S_0) + AsH_2 + H \quad \text{(Simmons and Beckman (273))}$$

$$Hg(6^3P_1) + CH_4 = Hg(6^1S_0) + CH_3 + H \quad \text{(Morikawa, Benedict, and Taylor (175))}$$
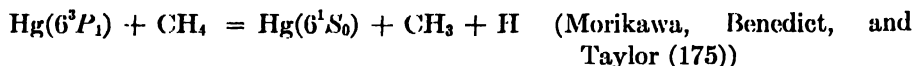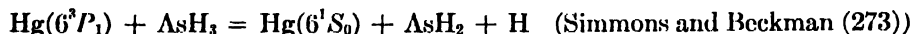
The method can obviously be used equally well for deuterium atoms (see references 75, 175, 285, and 293).

By using other metals as sensitizers it is possible to vary the energy input to the reacting molecule. Thus, with mercury, cadmium, and zinc the following excitation energies are involved:

SENSITIZER	EXCITATION ENERGY
	kcal.
Hg(6^1P_1) (1849 Å.)	153.9
Hg(6^3P_1) (2537 Å.)	112.2
Cd(5^1P_1) (2288 Å.)	124.4
Cd(5^3P_1) (3261 Å.)	87.3
Zn(4^1P_1) (2139 Å.)	133.4
Zn(4^3P_1) (3076 Å.)	92.5

In the case of cadmium (and probably zinc), however, there is one important difference. Olsen's work (187) makes it probable that with mercury hydrogen mixtures the primary step is a direct split into two hydrogen atoms, rather than an intermediate formation of mercury hydride. However, in the case of cadmium–hydrogen mixtures illuminated with the resonance line at 3261 Å., Bender (19) and Olsen have obtained strong resonance excitation of CdH bands. This indicates that CdH is formed in the normal state, and suggests that the primary step is

$$Cd(5^3P_1) + H_2 = CdH + H$$

It is, therefore, not at all certain *a priori* whether with reactions involving a C—H bond split in a hydrocarbon or other organic molecule, we have in a given case

$$M(^3P_1) + HX = M(^1S_0) + H + X$$

or

$$M(^3P_1) + HX = MH + X$$
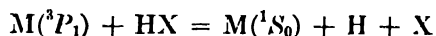
If the latter mechanism holds, the bond split will be less endothermic by an amount equal to the heat of formation of the hydride. Hence bonds may be broken which are "stronger" than the excitation energy of the metal atom by 8.5 kcal. in the case of mercury, 15.5 kcal. in the case of cadmium, and 23.1 kcal. in the case of zinc. There is no doubt that some cadmium-photosensitized reactions proceed in this way.

A number of investigations of reactions photosensitized by cadmium and zinc have recently been made (283). Some examples are given below:

REACTION	INVESTIGATORS
$Cd(5^3P_1) + C_2H_6$	Steacie and Potvin (297)
$Cd(5^3P_1) + C_3H_8$	Steacie, LeRoy, and Potvin (290)
$Cd(5^3P_1) + C_2H_4$	Bates and Taylor (15)
	Steacie and Potvin (298)
$Cd(5^1P_1) + C_2H_4$	Steacie and LeRoy (289)
$Zn(4^3P_1) + C_2H_4$	Steacie, Habeeb, and Le Roy (288)
$Zn(4^1P_1) + C_2H_4$	Steacie, Habeeb, and Le Roy (288)

An investigation of sodium photosensitization, using the D-doublet, has also been made by Jungers and Taylor (135). They found that ethylene quenched the radiation but was not chemically affected. The reason is, apparently, that the energy associated with this line (48 kcal.) is too small to cause decomposition or polymerization of ethylene.

3. Electrical

(a) Production of the active species by an electrical discharge

(1) The reactant is itself in the discharge: (For comprehensive recent reviews of the theory and chemical action of electrical discharges see references 101 and 321.)

There are two fundamentally different types of electrical discharge, the silent or non-disruptive discharge, and the disruptive discharge.

The silent discharge includes a number of types, such as the ozonizer, semi-corona, corona, glow, and electrodeless discharge. These have been used in numerous investigations with a variety of substances. There is no doubt that in many cases atoms and radicals are formed by the decomposition of organic or inorganic compounds. However, the situation is usually too complex to permit any accurate conclusions as to the rates of elementary reactions. On the other hand, the results are sometimes of value as confirmatory evidence for postulated mechanisms.

The disruptive discharges, the arc and the spark, are much more violent in nature. There is no doubt that the main effects of these discharges are thermal, and correspond to localized heating of the gas to 1500°C. or higher. In general, the results produced are so drastic that almost every possible atom or radical is produced by the discharge, and it is impossible to obtain much information about specific chemical reactions from work of this kind.

(2) *The products from a discharge are mixed with another substance: Hydrogen atoms*—As we have seen, atoms and radicals are produced in electrical discharges in gases. It was first shown by Wood (336, 337, 338, 339) that hydrogen atoms could be pumped out of a glow discharge in hydrogen and carried for considerable distances before they recombined. He found that for the success of the experiment it was essential that the walls of the tube be "poisoned" to slow down the recombination of the atoms, and that this could be done by a trace of water.

Following preliminary experiments by Taylor and Marshall (315a), Bonhoeffer (28, 29, 30, 31) modified Wood's apparatus and made extensive investigations of the chemical properties of atomic hydrogen. A typical apparatus for this kind of investigation is shown in figure 3. Hydrogen flows through a discharge tube carrying about 300 milliamperes at several thousand volts. By the use of a fast pump and large connecting tubing the rate of flow through the apparatus is made very high, about 3 meters per second; hence atoms are drawn out of the tube into the reaction vessel before much recombination has occurred. The other reactant is added through a jet leading into the reaction vessel. As in Wood's work, it is essential that the walls of the vessel be thoroughly poisoned to prevent catalytic recombination of the atoms. This can be done with water vapor, as used by Wood (for a modification see Trenner, Morikawa, and Taylor (324)), syrupy phosphoric acid (328), fused solid phosphoric acid (217), or potassium chloride (98). With efficient poisoning 20 to 50 per cent of hydrogen atoms may readily be obtained in the reaction vessel. The methods by which the hydrogen-atom concentration may be measured are described in a later section.

The pressures used are usually in the range 0.2 to 0.5 mm. With the pumping speeds employed, this is generally equivalent to a contact time of 0.5 to 1 sec. Under these conditions the rates of reactions involving hydrogen atoms can be

measured at room temperature, provided the activation energies are in the range 5 to 12 kcal.

The method has been used by a number of investigators at temperatures up to 180°C., and by Steacie up to 500°C. (282). At such high temperatures wall
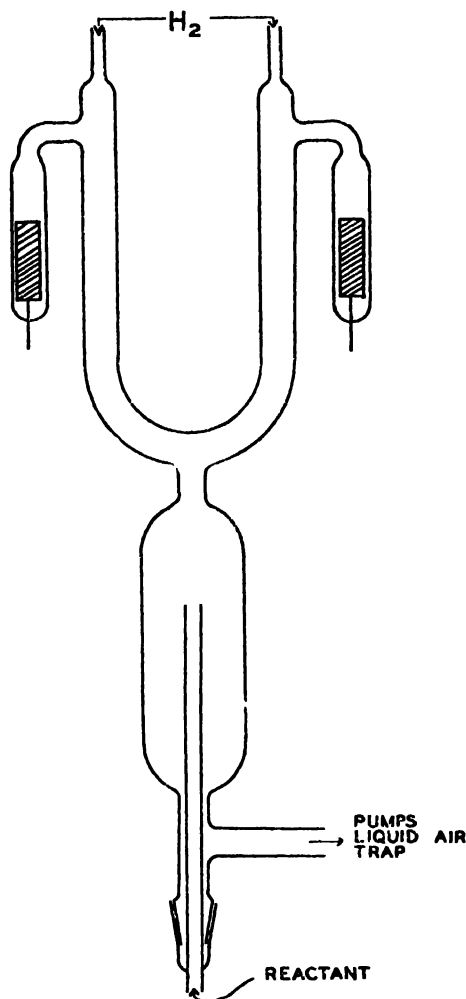
Fig. 3. Discharge-tube method for investigating the reactions of hydrogen atoms

poisoning becomes difficult, and only relatively low hydrogen-atom concentrations can be obtained (ca. 1 per cent). Reactions at liquid-air temperatures have been investigated by Geib and Harteck (95, 96).

The method has been modified by Harteck and Roeder (115, 116, 117). By adding an inert gas such as neon as a carrier, it was possible to operate the discharge at pressures up to 20 mm. The issuing mixture of hydrogen molecules,

hydrogen atoms, and neon could then be bubbled through liquids and the reactions of atomic hydrogen with dissolved substances investigated. (See, however, Klemenc (141) for a criticism of this method.)

In only a few investigations by the Wood–Bonhoeffer method have activation energies been determined from the temperature coefficient of the reaction in the ordinary way. The reason for this is that measurements of atom concentration are not very accurate, and since the reactions investigated have low temperature coefficients, these temperature coefficients cannot be accurately determined. In most cases, therefore, the investigations have been carried out at room temperature only. The results are then expressed in the form of a collision yield, calculated as the fraction of the number of collisions of a hydrogen atom with the reactant which are effective in causing reaction. The activation energy of the reaction is then usually estimated from the relation

$$x = Ze^{-E/RT}$$

where x is the collision yield, and Z is a steric factor, which is usually assumed to be equal to 0.1. This assumption is arbitrary, but is probably not far wrong in most cases, and the activation energies estimated in this way are thus usually reliable. If, however, a reaction happened to have a very small steric factor, say 10^{-4}, the activation energy estimated from the collision yield on the assumption that $Z = 0.1$ would be entirely misleading.

Surface effects probably constitute the main source of error in this method. It is practically impossible to estimate what fraction of the observed reaction may occur catalytically on the walls of the reaction vessel (75, 98).

A very large number of hydrogen-atom reactions have been investigated in this way (for a review see Geib (91)). Examples are the following:

$$H + H_2(para) = H_2(ortho) + H \quad (Geib\ and\ Harteck\ (94))$$

$$H + C_3H_8 = C_3H_7 + H_2 \quad (Steacie\ and\ Parlee\ (291,\ 292))$$

$$H + C_2H_2 = ? \quad (Bonhoeffer\ and\ Harteck\ (34))$$
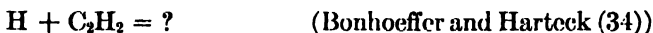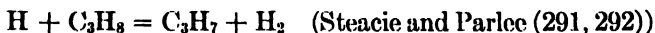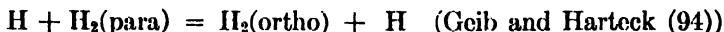
$$(v.\ Wartenberg\ and\ Schultze\ (327))$$

The method has been applied to deuterium-atom reactions by a number of workers (98, 107, 324); the results have been reviewed by Geib (92).

It is obvious that it would be possible to produce hydrogen atoms at higher pressures by means of a streaming method with an arc or spark discharge. However, under such circumstances the rate of flow would necessarily be relatively slow, the higher pressure would aid recombination of the atoms, and thus only minute quantities of atoms could be withdrawn from the tube. A very large number of claims of "active" modifications of hydrogen produced in this way have been made, but the results in all cases appear to be due to traces of impurity in the hydrogen.

Oxygen atoms—Wood's method has also been applied to oxygen by a number of investigators (10, 11, 24, 49, 253, 341). The main knowledge of oxygen-atom

reactions by this method comes from the work of Harteck and Kopsch (112, 113, 114) and of Geib (91), who used apparatus identical with that described above for hydrogen atoms. One complicating factor in dealing with oxygen-atom reactions is the formation of ozone by the reaction

$$O + O_2 (+ M) = O_3 (+ M)$$
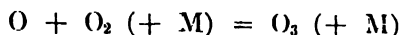
At low pressures and at temperatures from room temperature upward, however, this is relatively unimportant and the only "active" modification of oxygen present is atomic oxygen. Low-temperature investigations of oxygen-atom reactions have been made by Geib and Harteck (96, 97) and by Schenk and Jablonowski (259, 259a). Nalbandyan (177, 178) has produced oxygen atoms from a discharge and by sudden compression has obtained appreciable atom concentrations at relatively high pressures.

The hydroxyl radical—The presence of the hydroxyl radical can be demonstrated spectrographically in emission in the gas flowing from a Wood's tube with moist hydrogen (29), moist oxygen, or water vapor (153). Oldenberg (185) has succeeded in photographing the hydroxyl bands in absorption under similar conditions. However, the situation produced is highly complex, since we may have present also H, O, H_2O_2, HO_2, etc. As a result it is difficult to interpret the results obtained (87, 88, 113, 184, 185, 186, 304, 325, 333).

Nitrogen atoms—These can also be obtained by Wood's method (112, 340, 341, 259a).

Chlorine atoms—Rodebush and Klingelhoeffer (252) produced atomic chlorine by means of a high-frequency discharge. A flow system with a fast pump was used, and atomic chlorine could be pumped out of the tube for some distance. In this way concentrations of atomic chlorine up to about 20 per cent, as measured with a Wrede gauge, were obtained.

Schwab and Friess (265, 266, 267) have prepared atomic chlorine in concentrations up to 40 per cent by Wood's method. The atom concentration was measured calorimetrically. The main difficulty is to prevent too rapid recombination of the atoms on the material of the electrodes. They found that water-cooled iron electrodes gave the best results. On account of the very rapid recombination of the atoms on the walls of the apparatus (one collision in about twenty is effective), the results obtained are much more difficult o interpret than is the case with hydrogen atoms.

Bromine atoms—Schwab (264) investigated atomic bromine by Wood's method. It was found by calorimetric means that practically every collision of a bromine atom with the wall led to recombination, irrespective of the wall material. As a result, it was not possible to investigate reactions of atomic bromine with other substances.

Free radicals—Rice and Whaley (248) used Wood's method with a variety of organic compounds, viz., butane, pentane, ethylene, methanol, ethyl alcohol, acetaldehyde, acetic acid, and acetone. The products were passed over metallic mirrors in an attempt to identify the radicals produced. They found that the fragments removed antimony and lead mirrors, but not zinc or cadmium.

Hydrogen atoms were undoubtedly present, but the evidence points to radicals as well, although these were not definitely identified. The work would well merit extension.

(b) Production of the active species by collision with ions

The ions may be produced (a) by radioactive sources (164) or (b) by fast electrons (101). Many reactions occur under these influences, and the results obtained are of definite interest by comparison with photochemical and thermal reactions of the same substances. As yet, however, no information leading directly to the rates of elementary processes has been obtained in this way.

(c) Production of the active species by collision with slow electrons (of controlled speed)

It is obvious that if an electron with an energy of, say, 7 or 8 volts collides with a molecule and transfers its energy to it, reaction can occur. In principle it should be possible to investigate many interesting reactions by using electrons of controlled speed (101). Actually, however, it is found that energy transfers of this sort are not effective by mere "collision," but only occur when the molecule is raised to an excited state which may then dissociate. Thus with hydrogen the possible process

$$H_2 + E \text{ (4.31 volts)} = 2H + E$$
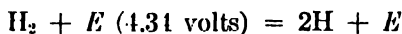
does not occur. Hydrogen, however, can be dissociated or excited by such processes as the following:

$$H_2 + E \text{ (11.6 volts)} = H_2^* = 2H + \text{kinetic energy}$$

$$H_2 + E \text{ (11.4 volts)} = H_2^*$$

$$H_2 + E \text{ (15.31 volts)} = H_2^*$$

$$H_2 + E \text{ (17.81 volts)} = H + H^*$$
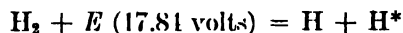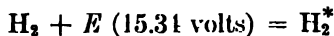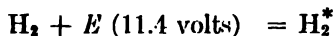
Such methods open up interesting possibilities in the investigation of the reactions of excited atoms and molecules. However, as yet no detailed information on ordinary elementary processes has been obtained from such work.

An interesting modification of the method is the investigation of mercury-sensitized processes by Glockler and Thomas (102). It was found that dissociation of hydrogen did not occur in the presence of mercury vapor and electrons of 4.9 volts energy, although it might have been expected by the mechanism

$$Hg(6^1S_0) + E \text{ (4.9 volts)} = Hg(6^3P_1)$$

$$Hg(6^3P_1) + H_2 = Hg(6^1S_0) + 2H$$
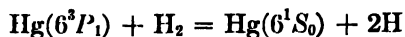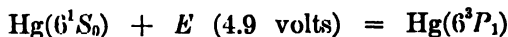
However, the hydrogen pressure used was very low (ca. 10^{-2} mm.), and almost all excited mercury atoms would radiate rather than be quenched by hydrogen.

With electrons of 7.7 volts energy dissociation of hydrogen occurred, presumably by the formation of metastable atoms by the following reactions

$$Hg(6^1S_0) + E \text{ (7.7 volts)} = Hg(7^3S_1)$$

$$Hg(7^3S_1) = Hg(6^3P_{0,2}) + h\nu$$
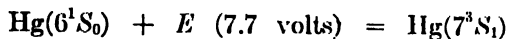
The metastable mercury atoms thus formed are then quenched by hydrogen to an appreciable extent on account of their relatively long life; i.e.,

$$Hg(6^3P_{0,2}) + H_2 = 2H + Hg(6^1S_0)$$
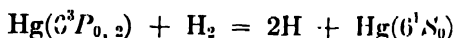
B. THE DETECTION AND ESTIMATION OF ATOMS AND RADICALS

The methods of detection and estimation of atoms and radicals may be classified as follows: (1) by chemical properties, (2) by spin-isomerization, isotopic labelling, etc., (3) by physical properties, (4) by optical methods, and (5) by inference.
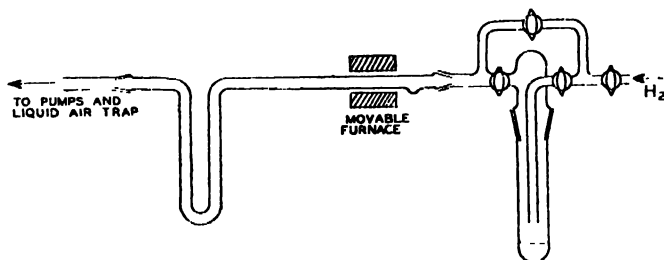
FIG. 4. The Paneth method of detecting free radicals

1. Chemical properties

(a) The removal of mirrors

It was first shown by Paneth and Hofeditz (1924) that free methyl radicals could be detected by their reaction with a metallic mirror deposited on the walls of a tube through which a carrier gas together with the radicals was flowing.

The apparatus is shown in figure 4. A stream of hydrogen which had been specially purified was passed at a low pressure, of the order of 1 to 2 mm., through a cooled vessel in which it was saturated with lead tetramethyl vapor, and was then led through a hard-glass tube. One end of this tube was heated with a Bunsen burner, or better, with an electric furnace (194), and in this the flowing lead tetramethyl was decomposed. The decomposition proceeded presumably by the reaction

$$Pb(CH_3)_4 = Pb + 4CH_3$$
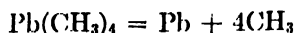
and a "mirror" of lead was deposited on the walls of the tube. If now the tube was heated "up-stream" from the lead mirror, it was found that the first mirror gradually disappeared, even if the distance was as great as 30 cm., although the rate of removal was slower the greater the distance. This is strong evidence

that the methyl radicals produced in the decomposition were removing the lead mirror by the reaction

$$4CH_3 + Pb = Pb(CH_3)_4$$
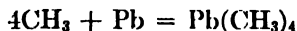
The success or failure of the method depends entirely on the speed of the pumping system, since it is essential to carry the methyl radicals along the tube for considerable distances before they disappear by the reaction

$$2CH_3 = C_2H_6$$
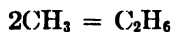
or other reactions. In Paneth and Hofeditz' work a fast diffusion pump was employed, which with a pressure of 1–2 mm. in the apparatus produced linear speeds through the tube up to 16 meters per second. At such speeds no diffusion against the flow occurred, and free lead was never deposited ahead of the heated zone.

Tests were made to prove that the phenomenon of mirror removal was not due to thermal effects produced by the stream of hot hydrogen. In the first place a flame very close to a lead mirror caused no effect when a stream of pure hydrogen (without lead tetramethyl) was used, other than a very slow creeping forward of the edge of the mirror. Secondly, water cooling of the tubing between the heated zone and the mirror did not prevent the removal of the mirror. (Direct cooling of the mirror itself by water often inhibited mirror removal, owing to the deposition on the mirror of traces of high-boiling substances.)

Tests showed that some lead tetramethyl passed the burner without decomposition, and in later work an electrically heated spiral of wire was wound round the tube just past the flame. Under these circumstances complete decomposition occurred.

Antimony and zinc mirrors were also used successfully.

Experiments were made by Paneth and Hofeditz to determine the lifetime of the free methyl radical. Antimony mirrors were deposited on the walls of the tube under controlled conditions, so that the same amount of metal was deposited in each case. (The experimental methods of obtaining such standard mirrors are not given in any further detail by Paneth and Hofeditz.) The mirrors in successive experiments were placed at different distances from the heated zone, and the time required for the removal of the mirrors was measured. In this way it was possible to follow the decrease in the concentration of methyl radicals as the distance from the heated zone was increased. In these experiments a streaming velocity of 14 meters per second was used, and the lead tetramethyl concentration in the stream corresponded to its vapor pressure at $-70°C$. The total pressure was approximately 2 mm. The results are given in table 6.

When $\log A$ is plotted against the distance, l, or the time, z, a straight line is obtained. In other words, the concentration of radicals, or activity, falls off with time according to a first-order law. This is illustrated by the data in table 7, in which the later values only are used, since the values with the mirror very close to the heated zone are not so reliable. In the table t is the time taken

by the radicals in travelling from $l = 13$ cm. to $l = l$, A_1 is the activity at $l = 13$ cm., and A_2 is that at $l = l$.   Whence we obtain

$$\text{Half-life} = 1/k_{\text{unimolecular}} = 5.8 \times 10^{-3} \text{ sec.}$$

The unimolecular nature of the "decay" is surprising, since it might be expected that the radicals would disappear by the reaction

$$2CH_3 = C_2H_6$$
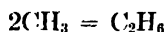
There are two obvious possible explanations: (a) The reaction

$$CH_3 + H_2 = ?$$
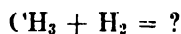
TABLE 6

DISTANCE, l, FROM HEATED ZONE TO MIRROR	TIME, z, TAKEN TO TRAVEL THIS DISTANCE	TIME, d, REQUIRED TO REMOVE THE MIRROR	ACTIVITY, A $A = \dfrac{1}{1000d}$	$\log_{10} A$
cm.	seconds	seconds		
4	2.9×10^{-3}	4	250.0	2.40
8	5.7	11	90.9	1.96
13	9.3	20	50.0	1.70
18	12.9	25	40.0	1.60
22	15.7	45	22.2	1.35
28	20.0	70	14.3	1.16
33	23.6	100	10.0	1.00
37	26.1	150	6.7	0.82

TABLE 7

Data illustrating the first-order loss of activity

l	z	t	A	$\log_{10} A_1/A_2$	$k = 1/t \ln_e A_1/A_2$
cm.	seconds	seconds			
13	9.3×10^{-3}	0	50.0		
22	15.7	6.4×10^{-3}	21.2	0.35	127
28	20.0	10.7	14.3	0.51	117
33	23.6	14.3	10.0	0.70	113
37	26.4	17.1	6.7	0.88	118

i.e., the methyl radicals disappear by reaction with hydrogen. This is in large excess, and hence the loss of radicals will follow a first-order law. (b) The radicals disappear by a first-order wall reaction. The obvious method of deciding between these is to use other carrier gases.

In a further paper Paneth and Lautsch (195) investigated the lives of the methyl and ethyl radicals when hydrogen and helium neon mixtures were used as carrier gases. The lives found were not very different in the two cases and they therefore drew the following conclusions: (a) Radicals do not disappear in hydrogen to an appreciable extent by the reaction

$$CH_3 + H_2 = CH_4 + H$$
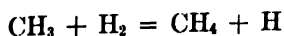
(b) At the pressures concerned three-body collisions are rare, and the recombination process

$$2CH_3 + M = C_2H_6 + M$$
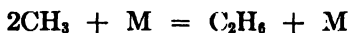
cannot be important. (c) Hence radicals disappear mainly at the wall. However, calculations show that by no means all collisions with the wall are effective in producing recombination (actually, only about one collision in one thousand is effective).

By using a "guard mirror" before the regular mirror and increasing its width in successive experiments, they found the maximum width of mirror necessary to remove all the radicals. These results indicate (191) that every collision of a radical with the mirror results in the formation of metalloörganic compounds.

Paneth and Lautsch also found that if a portion of the tube was cooled to −180°C. all radicals were removed. Hence, even with glass, the accommodation coefficient is approximately unity at very low temperatures. At higher temperatures the life increases, presumably because the accommodation coefficient decreases, up to about 500°C. At still higher temperatures the life decreases again. In helium at 500°C. the life of the methyl radical can be raised to 0.1 sec. (193).

Paneth and Lautsch also showed that iron and platinum had no catalytic effect on the recombination (see also Paneth (188)). Since iron removes atomic hydrogen, this proves that the effects found by Paneth and his coworkers with mirrors are not due to hydrogen atoms, as claimed by Schultze and Müller (260). They also found (194) that lead, arsenic, antimony, zinc, and cadmium mirrors were effective.

Precautions in the control of flow rates, etc., have been described by Paneth Hofeditz, and Wunsch (193).

Later work (193) seems to indicate that the wall effect was overestimated by Paneth and Lautsch, and that even at room temperature a fair amount of methyl disappears by the reaction

$$CH_3 + H_2 = CH_4 + H$$
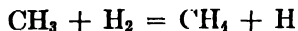
One further significant fact emerges from the work of Paneth, Hofeditz, and Wunsch. Lead tetramethyl was decomposed in the apparatus in the usual way. This deposited a lead mirror, which we may distinguish as mirror I. The alkyl radicals formed in the decomposition of the lead tetramethyl which resulted at the time of formation of mirror I reacted with a second mirror and formed lead tetramethyl again. This was decomposed again, and a new mirror, II, was formed. The amount of lead in mirror I was then compared with that in mirror II. The result found was that at low lead tetramethyl concentrations up to 82 per cent of the lead at mirror I was found at mirror II. Hence the yield of free methyl radicals on decomposing lead tetramethyl by the Paneth technique is almost 100 per cent.

Rice, Johnston, and Evering (238, 242) greatly simplified the experimental arrangement by substituting condensable gases for hydrogen or helium as

carriers. Using water vapor, carbon dioxide, or organic solvents as carriers, it is possible to freeze the carrier out with liquid air. Under these circumstances high-speed pumps are unnecessary. The simplified apparatus is shown in figure 5.

"A 1% solution of lead tetramethyl in acetone or heptane is put into tube A. The stopcock 1 is opened and the apparatus is evacuated. This automatically removes all oxygen from the apparatus and after one or two minutes the stopcock is again closed. The furnace is then heated to 500–600° and a metallic mirror is formed by heating a piece of metal which has previously been introduced into the quartz tube at C. The mirror is cooled with water, the stopcock 1 is opened, and the current of gas containing the free methyl groups is allowed to pass over the mirror."

"Numerous classes of organic compounds, such as hydrocarbons, ketones, ethers, etc., can be decomposed into free radicals in the apparatus shown in Fig. 2 (figure 5 in this paper). The vapor of the material itself is used as transport gas for the free radicals; the only modification in method, from that used when an organo-metallic compound is decomposed, is that the furnace must be heated to a higher temperature, usually in the range 750–950°C.
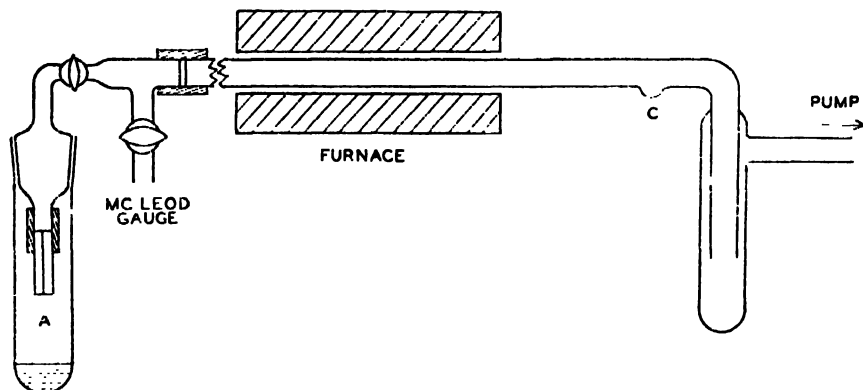
Fig. 5. The Rice apparatus for investigating free radicals

When using this apparatus for the decomposition of non-metallic compounds, the flask A containing the compound is evacuated for a few minutes so as to remove all air from the apparatus. The temperature of the flask and the size of the capillary are so adjusted that the vapor pressure at the inlet end of the quartz tube B is in the range 0.5 to 2 mm. A good oil pump, capable of producing a vacuum of 0.05 mm., is sufficient, although an auxiliary mercury vapor pump is desirable on account of the higher speed of evacuation."

Rice and his collaborators have shown (242) that a wide variety of metals may be used as mirrors: viz., lithium, sodium, potassium, calcium, zinc, cadmium, mercury, lanthanum, thallium, tin, lead, arsenic, antimony, bismuth, selenium, and tellurium. Negative results were obtained with magnesium, copper, silver, gold, and cerium.

In connection with the Paneth–Rice method, it should be noted that it is merely the standard flow method, except that the speed of flow is unusually high. The distinctive features of the work are the methods of detection of the radicals. As we shall see, the main difficulties associated with the application of the method to the determination of the activation energies of elementary reactions arise in

connection with the methods of detection, which are a matter of very great experimental difficulty.

Paneth and Hofeditz found that the mirrors often lost their activity if the tube was cooled by running water, owing to the deposition on the mirror of traces of high-boiling substances which prevented the access of radicals to the mirror. Mirrors may also be formed, and more conveniently, by introducing a small pellet of metal into a small depression in the tube, and heating the tube at this point with a current of gas flowing through it. Some of the metal is thus volatilized and deposited "down-stream" as a mirror on the colder parts of the apparatus.

It is essential that all air be excluded from the apparatus, since a trace of oxygen will deactivate the mirror, presumably by forming an oxide layer on the surface.

In using "standard mirrors" Paneth and Lautsch (195) encountered considerable difficulty in obtaining reproducible results. It was not possible to reproduce each time the surface condition of the mirrors, even though they contained the same quantity of metal. The difficulty was less, but still considerable, in new glass or quartz tubes. In consequence they reported their results as only provisional in a quantitative sense.

Paneth and Hahnfeld (190) found that results with tellurium were much more reproducible, since tellurium mirrors are not inactivated by traces of oxygen as are mirrors of other metals. They determined the activity not by the time for the removal of a mirror, but by its loss in weight. Details of their procedure were not given.

The use of tellurium mirrors was extensively investigated by Rice and Glasebrook (235). They also pointed out (233, 234) that in some cases mirrors are definitely specific in action. Thus methylene removes tellurium, antimony, selenium, and arsenic, but does not attack zinc, cadmium, bismuth, thallium, or lead, all of which are readily removed by alkyl radicals. The effect was shown by experiments in which the removal of mirrors was investigated, using the products of the decomposition of ether and of ether–diazomethane mixtures. The pyrolysis of ether yields methyl radicals, while that of diazomethane gives methylene. It was found that there was very little difference in the rate of removal of zinc mirrors on substituting an ether–diazomethane mixture for pure ether. However, antimony and tellurium mirrors were removed much more rapidly with the ether–diazomethane mixture. The results are illustrated by figures 6 and 7 (reproduced from Rice and Rice (242)).

Rice and his collaborators (242) also investigated the effect of the temperature of the mirror on its activity. They found that the activity of lead mirrors diminished rapidly at higher temperatures. Thus, a mirror which was removed in about 20 sec. at room temperature required over 200 sec. at 325°C. under the same conditions of radical concentration, etc. In agreement with Paneth and Hofeditz, they found that lead mirrors were frequently inactivated by cooling to 0°C., presumably owing to the deposition of traces of gummy materials on the mirror. In the case of antimony mirrors the activity remained approximately constant up to high temperatures.

Rice and Johnston (237) used the standard mirror technique to investigate the activation energy of the decomposition of organic substances into free radicals. The organic compound was passed through a furnace under conditions such that only a small fraction of it decomposed. A standard mirror was placed at a definite distance from the end of the furnace and its time of removal was noted. The furnace temperature was then varied, and the time of removal of similar mirrors was determined as a function of the furnace temperature.
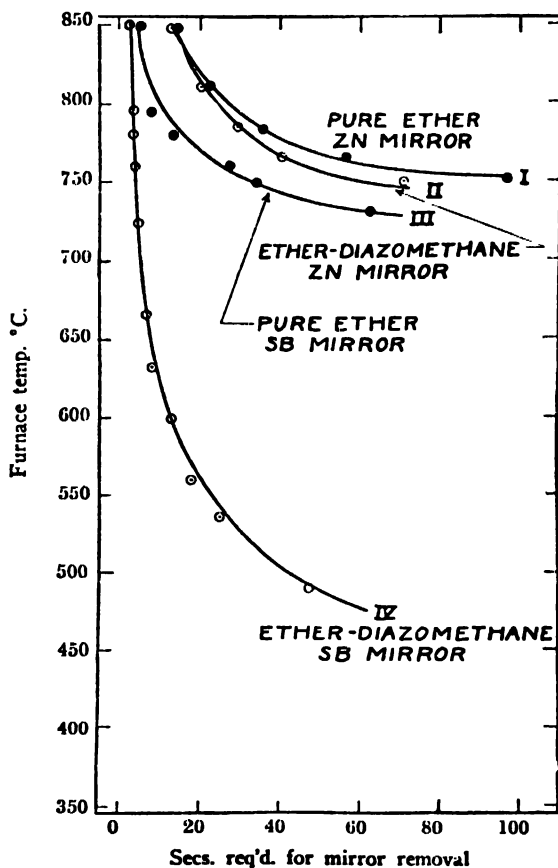
FIG. 6. The removal of zinc and antimony mirrors by methyl and methylene radicals

Since the removal time of the mirror is a measure of the radical concentration, and since this concentration is for small fractional decompositions a measure of the rate constant of the decomposition, we can thus determine the temperature coefficient of the split into free radicals, and the activation energy.

Glazebrook and Pearson (100, 207) found that mirrors, including those of tellurium, were deactivated by traces of oxygen. They also found that the activity diminished on standing, owing perhaps to the gradual evolution of oxygen from the walls of the apparatus, or to crystallization of the metal. In

depositing standard mirrors Pearson used a smoked-glass tube as a comparison standard and measured the opacity (206, 209).

Prileshajeva and Terenin (220) adapted the Paneth technique by determining the rate of disappearance of the mirror by measuring its opacity photometrically. They found an induction period in the mirror removal, probably owing to the necessity of removing adsorbed gas before the mirror itself could be attacked.

In order to make the Paneth test more sensitive, Leighton and Mortensen
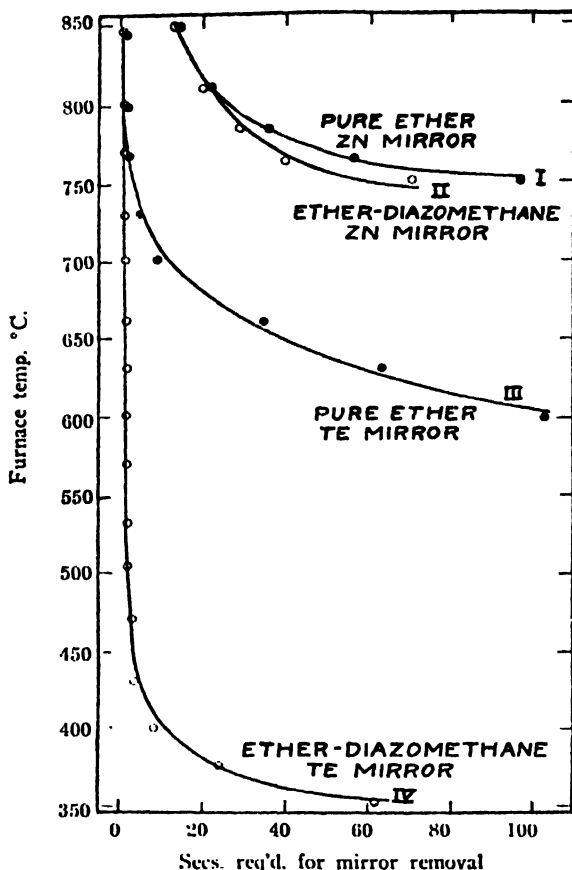
Fig. 7. The removal of zinc and tellurium mirrors by methyl and methylene radicals

(157) used lead containing radium D, radium E, and radium F (from old emanation tubes). A beta-ray electroscope was placed above the "mirror," which was so thin as to be invisible, and the disappearance of the mirror was followed by the loss of beta-ray activity. A liquid-air trap was placed in the line following the reaction tube, and its contents were also examined for beta-ray activity. They thus succeeded in detecting methyl radicals from the photolysis of lead tetramethyl. It was observed that only radium D (a lead isotope) was carried over, while radium E (a bismuth isotope) was not.

The radioactive-indicator method was also employed with modifications by Burton, Ricci, and Davis (41). They used a radium D mirror, and put the gases passing the mirror through a cracking furnace at 100° to 500°C. This decomposed the lead tetramethyl formed by the attack of methyl radicals on the mirror. The lead resulting from the decomposition of the lead tetramethyl carried over was then examined for radioactivity by cutting out the section of the tube where it deposited, dissolving the lead in hot nitric acid, and evaporating the solution to dryness. The lead nitrate formed was then examined with a Lind electroscope. They announced that further work was in progress, using radioactive antimony.

TABLE 8

Substances tested as detectors for free radicals

POSITIVE RESULTS		NEGATIVE RESULTS	
Substance	References	Substance	References
Lead	(192, 239)	Oxides*	
Bismuth	(192, 239)	Benzoic acid	(195)
Lithium	(239)	Copper	(239)
Calcium	(239)	Gold	(239)
Mercury	(239)	Mercurous chloride	(239)
Arsenic	(239)	Magnesium	(239)
Iodine	(16, 17, 18)	Silver	(239)
Antimony	(192, 239)	Cerium	(239)
Sulfur	(192)	Mercurous bromide	(239)
Sodium	(239, 271)	Lead chloride	(239)
Tin	(239)	SnI_3	(239)
Lanthanum	(239)	Eosin	(239)
Selenium	(239)	Lead iodide	(239)
Zinc	(192, 239)	Indigo	(239)
Tellurium	(195, 239)		
Potassium	(239)		
Cadmium	(239)		
Thorium	(239)		
Carbon tetraiodide	(274)		

* It may be inferred that most oxides are ineffective, since mirrors are inactivated by traces of oxygen.

Pearson, Robinson, and Stoddart (212) have shown that the Paneth technique may be used to detect hydrogen atoms. They found that atomic hydrogen removed arsenic, antimony, selenium, tellurium, germanium, and tin mirrors, but did not affect lead or bismuth, except for a slow movement down the tube with bismuth due to distillation. This effect did not occur with lead. Burton (39, 40) has improved the method and has used it to detect hydrogen atoms in photolyses. A heavy lead "guard mirror" was deposited first, followed by a very light antimony mirror. The guard mirror served to remove alkyl radicals, and thus allowed only hydrogen atoms to pass. These removed the antimony mirror. The method has been used by Burton and his collaborators in a number of cases (125, 168).

A large number of rather varied substances have been tried as detectors for free radicals by the mirror technique, as shown in table 8.

Kohanenko (143) has used screens of zinc sulfide instead of mirrors to detect atoms and radicals. These screens glow when atoms or radicals recombine on them.

(b) The estimation of the products resulting from mirror removal

For reviews of this subject see references 207 and 242.

Paneth and Hofeditz (192) identified the methyl radical in their original experiments by passing the gas over zinc mirrors and characterizing the zinc dimethyl formed by its melting point, boiling point, and spontaneous combustion in air with the formation of zinc oxide. They also roughly identified the antimony alkyls formed when antimony mirrors were used. Paneth and Lautsch (194) identified the ethyl radical similarly. They also partially oxidized

TABLE 9

Products formed by the reaction of free alkyl radicals with mirrors

METAL	PRODUCTS					
Lead	$Pb(CH_3)_4$	$Pb(C_2H_5)_4$				
Arsenic	$As(CH_3)_3$	$As(C_2H_5)_3$	$[As(CH_3)_2]_2$	$[As(C_2H_5)_2]_2$	$(AsCH_3)_s$	$(AsC_2H_5)_s$
Antimony	$Sb(CH_3)_3$	$Sb(C_2H_5)_3$	$[Sb(CH_3)_2]_2$	$[Sb(C_2H_5)_2]_2$*		
Bismuth	$Bi(CH_3)_3$	$Bi(C_2H_5)_3$	$[Bi(CH_3)_2]_2$			
Selenium	$Se(CH_3)_2$	$Se(C_6H_5CH_2)_2$	$(SeCH_2)_x$			
Tellurium	$Te(CH_3)_2$	$Te(C_2H_5)_2$	$(TeCH_3)_x$*	$(TeCH_2)_x$*		
Zinc	$Zn(CH_3)_2$	$Zn(C_2H_5)_2$				
Mercury	$Hg(CH_3)_2$	$Hg(C_2H_5)_2$	$Hg(C_3H_7)_2$	$(HgCH_4)_2$	$Hg(C_6H_5)_2$	$Hg(C_6H_5CH_2)_2$
Beryllium	$Be(CH_3)_2$	$Be(C_2H_5)_2$				
Iodine	CH_3I	C_2H_5I	CH_2I_2			

* Products formed only with warm mirrors.

the zinc ethyl to $C_2H_5OOZnC_2H_5$, hydrolyzed this, and identified the resulting ethyl alcohol by the iodoform test.

Sodium has also been used for identification purposes by Simons and Dull (274). The free radicals (methyl or ethyl) were allowed to come in contact with metallic sodium, forming a sodium alkyl. The mixture of sodium and sodium alkyl was treated with alcohol, whereupon methane was evolved in the case of methyl, or ethane in the case of ethyl.

Simons and Dull also used carbon tetraiodide as a detector. Methyl radicals formed methyl iodide, which was allowed to react with quinoline, and the resulting quinoline methiodide was identified.

The products formed when free alkyl radicals react with a variety of mirrors have been summarized by Rice (242) and by Pearson (207), and are given in table 9. The information comes from a variety of sources (16, 17, 18, 100, 189, 197, 208, 209, 210, 228, 232, 234, 238).

The main difficulty in all this work is the very small amount of product which must be identified. In identifying the radicals from hydrocarbon decompositions Rice, Johnston, and Evering (238) developed a technique which

has been widely used. The organometallic compounds formed by the interaction of radicals with metallic mirrors were caught in a liquid-air trap. It is very difficult to identify the compounds thus obtained, since they are mixed with a very large excess of other substances. The following procedure was therefore adopted: The radicals from the heated zone were brought into contact with a water-cooled surface on which mercury was continually condensing. In this way mercury alkyls were formed, and these were condensed in a liquid-air trap. The trap contained a few cubic centimeters of a saturated alcoholic solution of mercuric bromide. By this method alkylmercuric bromides were obtained in quantities up to about 1 g. After the material had been freed from excess mercury, etc., the residue was sublimed in a vacuum below 50°C. for an hour or two, and was thus separated from the less volatile excess of mercuric bromide. The alkylmercuric bromides were then separated by fractional sublimation. In ths manner the results shown in table 10 were obtained from the radicals formed in the decomposition of butane. The authors were unable to obtain

TABLE 10

Alkylmercuric bromides obtained from the radicals formed in the decomposition of butane

FRACTION	TIME OF SUBLIMATION	TEMPERATURE OF SUBLIMATION	YIELD	MELTING POINT
	hours	°C.	grams	°C.
1	1.0	10	0.217	157
2	1.0	50	0.161	160.5
3	1.5	50	0.110	172
4	1.5	50	0.048	181.5
5	1.0	60	Trace	

Melting point of $CH_3HgBr = 160°C.$, of $C_2H_5HgBr = 193.5°C.$, of $HgBr_2 = ca.\ 235°C.$

any indications of propylmercuric bromides. The above mixture appears definitely to consist of methyl- and ethyl-mercuric bromides (however, see later). By comparing the melting points of the fractions with those of known mixtures of methyl- and ethyl-mercuric bromides, they estimated that the ratio of methyl to ethyl radicals produced from butane was 7:3 Similar results were obtained with radicals from the pyrolysis of propane. Rice, Johnston, and Evering referred to a later publication by Rice and Whalley in which x-ray determinations were used to confirm the presence of methyl- and ethyl-mercuric bromides. The results of this work (248), however, seem rather equivocal.

Rice and Evering (232) repeated the above experiments and ran into considerable difficulty. They concluded that at least 95 per cent of the alkylmercuric bromides was methylmercuric bromide, and that ethylmercuric bromide was absent. The higher melting substance obtained in the previous work was presumably a small amount of mercuric bromide. In addition, they found that a trace of some unstable mercury alkyl is formed, probably $CH_3HgHgCH_3$. This is presumably the source of $HgBr$, a small amount of which was also detected. No indications of any methylene compounds were

obtained. Direct tests for the presence of ethyl groups were also made by a method developed by Willstätter and Utzinger (334), and these also were negative. Apparently then, only methyl radicals are detectable in the decomposition of propane and of butane. An improved technique for the identification of alkylmercuric halides has since been devised by Rice and Rodowskas (243). In this the mixture of alkylmercuric bromides and excess mercuric bromide is steam distilled. This effects a complete separation of the alkylmercuric bromides from the mercuric bromide, which is non-volatile under these conditions.

The fact that ethyl radicals are not detected in the decomposition means merely that higher radicals are unstable at high temperatures, and does not mean that the method is unsuitable for their detection. As a matter of fact, both ethyl and propyl radicals from photolyses have been identified by this technique by Pearson and his coworkers (209, 210). However, the above description will emphasize the difficulties encountered in work of this kind.

The products obtained from tellurium mirrors have also been widely employed for identification purposes, and have been the subject of much controversy. In particular, there has been much argument as to the existence of the methylene radical as deduced from evidence with tellurium and iodine mirrors. Since the question is of fundamental importance in connection with free-radical mechanisms, it will be reviewed in some detail, especially from the point of view of the occurrence or non-occurrence of the methylene radical in pyrolyses.

Rice and Glasebrook (235) investigated the free radicals produced from the decomposition of butane by means of tellurium mirrors, and found that the only detectable product was dimethyl ditelluride, $CH_3TeTeCH_3$. This is a deep red liquid with a low vapor pressure at room temperature; it is stable in air and melts at $-19.5°C$. This substance was recovered in almost theoretical yield in their experiments, and its composition was confirmed by combustion analysis. Similar results were obtained with radicals from acetone, in which case there is no doubt that methyl radicals are formed. This appears to confirm the idea that only methyl radicals are produced, ethyl and propyl radicals presumably being decomposed at the high temperatures used. They obtained no evidence of the presence of methylene.

Rice and Dooley (230) investigated the production of radicals when methane was decomposed at 1200°C. They obtained only pure dimethyl ditelluride, with no sign of telluroformaldehyde, $(TeCH_2)_x$, which would be expected if methylene radicals were present. This points definitely to the presence of methyl and the absence of methylene. (It is, of course, possible that the methyl radicals might be produced from methylene in secondary reactions.)

The methylene radical from the decomposition of diazomethane was identified by Rice and Glasebrook (230, 234), using tellurium mirrors. The product was a dark red solid of such low volatility that it condensed on the walls of the tube just beyond the mirror. Analysis showed it to have the empirical formula CH_2Te, i.e., it was telluroformaldehyde, probably in a highly polymerized state. The substance is insoluble in ordinary solvents, and decomposes at temperatures

above 100°C. It appears to be totally different from dimethyl ditelluride, and thus the use of tellurium offers a method of distinguishing between methyl and methylene radicals.

The work of Belchetz and Rideal is in sharp contrast to that of Rice and his coworkers. Belchetz (16), in a preliminary communication, reported that when methane was passed rapidly at a pressure of 0.1 mm. over a platinum filament at temperatures from 877° to 1027°C., tellurium mirrors situated one mean free path away were attacked. The products were collected in a liquid-air trap. Similar experiments were made with iodine mirrors. As a result of this work Belchetz concluded that methylene was the only primary product of the methane decomposition. Rice and Dooley were unable to obtain any mirror removal at such temperatures, even with platinum foil in their heated quartz tube. There seems to be little doubt that Belchetz' results were in error, since the temperatures used were impossibly low for a rapid-flow system unless there was a highly efficient catalytic effect due to the platinum. Also, as far as the identification of the products was concerned, Belchetz and Rideal were unable to confirm any of the results of the first paper. We may, therefore, disregard the results in the first paper and consider only Belchetz' later work.

Belchetz and Rideal (17) employed two different types of apparatus. In both of these the gas streamed through at a high velocity and at 0.1 mm. pressure. In the first the radicals formed on the hot filament were caught on a water-cooled target 3 mm. away. Mirrors could be deposited on this target, and any products formed were caught in a liquid-air trap. In the second apparatus the mirror was on the wall of the reaction vessel opposite the filament. It was considerably farther from the filament, and the system thus resembled the hot-tube type of apparatus employed by Paneth and by Rice. Tellurium and iodine mirrors were used, and carbon and platinum filaments. Methane was first investigated. With tellurium mirrors and platinum filaments, no volatile tellurium compounds were obtained. With platinum filaments and an iodine mirror, methylene iodide was formed.

Most of the work was done with carbon filaments. With iodine mirrors the identification of methylene iodide was claimed. This identification was attempted by two methods: In the first the substance was dissolved in chloroform, shaken with mercury to remove excess iodine, filtered, the chloroform evaporated off, and the product oxidized to formaldehyde and tested by the Schryver–Rimini test. For a minute quantity of material of dubious purity, such a complicated set of operations is hardly above suspicion. Attempts were also made to form mercury addition compounds, such as $HgCH_2I_2$, and to identify them, but these were unsuccessful. No methyl iodide was found, the search for it being made merely by means of its volatility. When, however, the filament was moved 1 cm. from the mirror, the yield of methylene iodide became negligibly small, and an unidentified liquid which might have been methyl iodide made its appearance in traces in the trap. (This seems a very abrupt change on merely increasing the distance by a factor of 3, especially since the radicals were not in a heated zone.)

Experiments with tellurium mirrors were also carried out. With the second apparatus described, dimethyl ditelluride and dimethyl telluride were obtained. With the first apparatus the products were found to accumulate on the mirror, where they were exposed to further reaction. If the mirror was kept at 100°C., the products formed distilled off and were collected in the liquid-air trap. Under these conditions a trace of methyl tellurides was obtained, together with large quantities of a yellow solid which was assumed to be the telluroformaldehyde of Rice and Glasebrook. Belchetz and Rideal concluded, "These experiments indicate that methyl radicals are very readily produced in the flow experiments, but are essentially secondary products. Apart from the readiness with which methylene takes up atomic hydrogen, telluroformaldehyde is liable to be reduced by atomic or even possibly by hot molecular hydrogen."

The whole question is controversial, and other work of Belchetz and Rideal (18) also disagrees with Rice's findings. Thus with propane, using tellurium mirrors and carbon filaments, they found small amounts of dimethyl ditelluride and of telluroformaldehyde with warm tellurium mirrors, but only methyl tellurides with cold tellurium mirrors. They suggest that this is due to reduction of telluroformaldehyde by hydrogen when it remains in contact with a cold mirror, while with the warm mirror it evaporates off quickly and thus is not reduced. (There is also the possibility that with warm mirrors the reverse of this reaction might occur, i.e.,

$$CH_3 + CH_3Te = CH_4 + CH_2Te$$
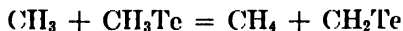
or some such process.)

With mercury mirrors Belchetz and Rideal obtained large amounts of mercury alkyls, which with mercuric bromide gave CH_3HgBr. No ethylmercuric bromide was found, in agreement with the work of Rice and Evering. They attributed the formation of methylmercuric bromide to the sequence

$$Hg + H + CH_2 = HgCH_3 \tag{1}$$

$$2HgCH_3 = Hg(CH_3)_2 + Hg$$

Reaction 1 seems exceedingly unlikely when the low pressure and very short reaction time are taken into consideration. Also, throughout all this work Belchetz and Rideal spoke of the atomic hydrogen present, but on the basis of their mechanism where does it come from? After all, there is no hydrogen in the reactant, and in one mean free path it cannot very well be formed by secondary processes.

Belchetz and Rideal concluded that, "In view of the experience of Rice and Glasebrook with the decomposition of diazomethane in the presence of butane or ether at temperatures above 650°C., when only methyl and no methylene radicals could be detected, it is not unlikely that all the methyl radicals formed in hot-tube decompositions of the hydrocarbons are in reality only secondary products of methylene."

It will be seen from the above that there are great difficulties in the unequivocal

identification of free radicals in some cases, and that considerable caution is necessary in the interpretation of the results. However, there seems to be no question that the methylene radical has been detected in certain cases.

Paneth and Lautsch (196) made numerous unsuccessful attempts to identify free methylene. These included the thermal decomposition of ketene and of diazomethane, an electrical discharge in diazomethane, and the reaction between dichloromethane and sodium (120):

$$CH_2Cl_2 + 2Na = 2NaCl + CH_2$$
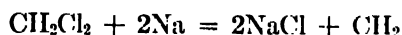
All these attempts failed, but the failure was probably due to the detectors which they chose, namely, benzoic acid and carbon, neither of which would be expected to react very readily with methylene.

Rice and Glasebrook (233, 234) investigated the decomposition of diazomethane by their usual technique. Diazomethane with ether or butane as a carrier was passed through a tube at 550°C. or less, and then over mirrors. It was found that tellurium, selenium, arsenic, and antimony mirrors were readily removed, whereas zinc, cadmium, thallium, lead, and bismuth mirrors were not affected. In the case of tellurium mirrors the product was found to be a polymer of telluroformaldehyde, $(TeCH_2)_n$. This was a non-volatile red solid which condensed on the walls just beyond the mirror. At temperatures higher than 600°C. it was found that no telluroformaldehyde was produced, but only dimethyl ditelluride, $CH_3TeTeCH_3$, i.e., the methylene radicals were replaced by methyls. This work appears to give a very distinct test for methylene. The combustion data given to confirm the constitution of telluroformaldehyde were as follows:

	Per cent carbon	Per cent hydrogen
Calculated for CH_2Te	8.40	1.41
Found for CH_2Te	8.28	1.33

It should be noted, however, that on account of the high weight of the tellurium atom, virtually any organic tellurium compound would give a similar carbon analysis. The hydrogen analysis, though rather rough, is significant, since the per cent of hydrogen for the formula $Te_2(CH_3)_2$ would be 2.01. Actually, the calculated carbon value is in error, since the per cent of carbon for the formula CH_2Te is 8.47. The agreement is thus not quite as good as indicated above, although a small amount of occluded tellurium would account for the difference.

Rice and Glasebrook also found that at low temperatures no radicals were produced which would react with mercury to form mercury alkyls, but that at high furnace temperatures mercury dimethyl was formed.

They pointed out that telluroformaldehyde is so non-volatile that the compound found by Belchetz and Rideal cannot be it. Belchetz and Rideal suggested that in their work telluroformaldehyde came over as the monomer and polymerized in the trap. This, however, offers no explanation of the distinct difference between the compounds found in the two investigations.

Rice and Glasebrook concluded that the disappearance of methylene radicals

and appearance of methyl radicals at higher temperatures is satisfactorily explained provided the reaction

$$CH_2 + C_4H_{10} = CH_3 + C_4H_9$$
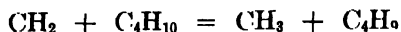
or the corresponding reaction with ether has an activation energy of about 15 ± 5 kcal.

In a review article Rice (228) referred to further unpublished work, carried out in collaboration with Bongiorni, which cast doubt on the work of Rice and Glasebrook described above. They reported as follows: "Cold diazomethane vapor appears to react with the tellurium vapor over a hot tellurium mirror to form telluro-formaldehyde. When experiments were performed under conditions such that this error was avoided, only methyl groups came out of the furnace. Thus even with pure diazomethane in pure nitrogen, methyl groups were obtained and carbon was deposited in the furnace." It appears from this work that Rice and Glasebrook's detection of the methylene radical was fallacious. However, the work of Bongiorni has never been published, a fact which suggests that it was not confirmed by later investigations.

A rather thorough investigation of this question was later made by Pearson, Purcell, and Saigh (211). They investigated both the thermal and the photochemical decomposition of ketene, using the mirror-removal technique. It was found that ketene irradiated with a hot or cold mercury arc had no effect on a cold tellurium mirror. However, if the mirror was heated to 70–80°C., it was readily removed. Blank experiments showed that this was not due either to evaporation or to an attack by ketene itself on the mirror. These authors suggested, as had others, that the necessity for heating the mirror is to prevent the formation on it of a layer of polymer.

They were unable to obtain the red telluroformaldehyde of Rice in a simple way. However, if the tube downstream from the mirror was cooled to $-80°C.$, the compound described by Rice was obtained (although they called it a deep orange, while Rice described it as red). It was found that the cooling was necessary only for seeding purposes, since if the tube was cooled for only a short time, the material continued to form where the cold spot had been.

Pearson, Purcell, and Saigh also obtained a gray substance which they took to be another modification of telluroformaldehyde. This, in solution with iodine, formed a substance which was fairly definitely proved to be methylene iodide. They also obtained evidence of the presence of an addition compound of the approximate constitution $TeCH_2 \cdot 12.5CH_2CO$. They concluded: "It is evident, therefore, that telluro-formaldehyde is first generated as a gas, which undergoes the familiar aldehydic condensations to a white form and a red form, the latter in view of its solubility being the higher polymer." They obtained no evidence of the presence of methyl radicals.

In a similar way selenium mirrors, even when cold, were readily removed with the formation of selenoformaldehyde.

The products from the thermal decomposition and the photodecomposition of diazomethane in the presence of tellurium mirrors were also investigated, and appeared to be telluroformaldehyde as before.

Pearson and coworkers concluded that, since one form of telluroformaldehyde is volatile, Rice's criticism of Belchetz and Rideal's results on the ground that it could not have escaped into the liquid-air trap cannot be upheld.

In a recent brief note (229) Rice described some further work. "We have attempted to obtain methylene from methane and other hydrocarbons by passage over heated filaments in an apparatus similar to that used by Belchetz and Rideal. Under their conditions for detecting methylene (Fig. 1 of reference 17), we succeeded in removing tellurium mirrors, but were unable to obtain enough tellurium compound to identify: we found that even after runs of several days, the amount of tellurium removed could not be weighed on an ordinary analytical balance. (Rice does not say whether the tellurium mirrors were heated or not.)

"On the other hand, by using much longer wires (Fig. 2 of reference 17) and larger mirrors, our results agreed with those reported by Belchetz and Rideal, and were similar to those obtained by passing methane through a quartz furnace; dimethyl ditelluride was obtained and identified by its melting point at $-19.5°C$."

The whole question of the existence and identification of methylene has been reviewed by Barrow, Pearson, and Purcell (12). They reviewed the foregoing evidence at some length and concluded: "It seems to us that the fairest conclusion that can be drawn is that methylene as well as methyl may be one of the primary products in the dissociation of methane. Methylene radicals so formed may then undergo a rapid reaction with either methane, hydrogen, or another methylene radical, resulting in the production of methyl radicals. This cautious conclusion is dictated by our knowledge of the difficulties inherent in the unambiguous identification of products from experiments with filaments at low pressures, by the absence of quantitative data concerning the extent to which the dissociation of the hydrocarbons proceeds via a mechanism involving free radicals, and the equivocal nature of the evidence which may be adduced from kinetic experiments."

This seems a fair summing up of the situation as far as the detection of radicals is concerned. However, Barrow, Pearson, and Purcell overlook some of the kinetic evidence which is by no means "equivocal." In work with ethane, propane, and butane Belchetz and Rideal obtained in all cases an activation energy of ca. 94 kcal., and concluded that in every case the primary process was a direct molecular split and did not involve free radicals. This activation energy is much above the activation energies of the over-all thermal decompositions (60 to 70 kcal.). Now if free radical chains exist in these reactions, as postulated by Rice, there is every reason why the primary free radical split should have an activation energy 10 to 20 kcal. higher than that of the over-all reactions. If, however, as Belchetz and Rideal suggest, radicals are not involved, and the primary process is a direct molecular split into the final products, then there is no reason for the discrepancies in the activation energies. It therefore seems certain that in all of Belchetz and Rideal's work the carbon filament was a complicating factor, as they themselves realized. Furthermore, the fact that the activation energies are the same, within the experimental error,

for methane, ethane, propane, and butane suggests that the primary step is a direct reaction of some sort with the carbon filament. In any case, it appears clear that while Belchetz and Rideal's work may have a bearing on the question of the detection of the methylene radical, it has no bearing whatsoever on the homogeneous decomposition of hydrocarbons in the gas phase.

Barrow, Pearson, and Purcell also reviewed the evidence for ethylidene in the dissociation of ethane, in the light of the work of Rice and Dooley (230), who detected methyl radicals, and of Belchetz and Rideal who claimed ethylene and hydrogen as the primary products, possibly with ethylidene as an intermediate. In addition, there is evidence from work on the decomposition of diazoethane. Rice and Glasebrook (235) decomposed diazoethane at 650°C. and found no evidence of ethylidene, but rather of ethylene. Barrow, Pearson, and Purcell reported that at lower temperatures (400–450°C.) radicals were obtained which combined with selenium and tellurium to yield compounds with properties resembling those of seleno- and telluro-acetaldehydes. At 600°C., however, they obtained no mirror removal. It appears likely, therefore, that the ethylidene radical has been detected.

(c) Reactions in the gas phase

Free radicals have been detected by gas-phase reactions with the halogens in a number of cases. Thus Horn, Polanyi, and Style (130) formed methyl radicals by the reaction

$$CH_3Br + Na = NaBr + CH_3$$
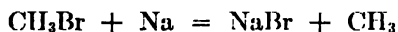
The methyl radicals were then identified by introducing them into chlorine or iodine and identifying the methyl chloride or iodide formed. Similar experiments have been carried out with ethyl and phenyl radicals (129).

Gorin has used iodine to "fix" radicals and hydrogen atoms in a number of cases (103, 104, 105). In photolytic experiments iodine was mixed with the reactant. Any hydrogen atoms formed were "fixed" as hydrogen iodide, and alkyl radicals as methyl iodide, ethyl iodide, etc. In this way it was possible to determine the atoms or radicals formed in the primary reaction.

In a number of cases free radicals have been detected by the effects caused by their removal by gas-phase reactions. Nitric oxide has been the most widely used reagent for this purpose. Hinshelwood and his coworkers (127a, 128a, 128b, 281, 281a, 281b, 281c, 281d, 281e) have found that a number of reactions which are suspected to proceed by free-radical chain mechanisms are inhibited by the addition of small amounts of nitric oxide. The function of the nitric oxide is presumably to remove the radicals, and thus to prevent the further propagation of chains involving them. The nitric oxide probably forms an addition compound

$$R + NO = RNO$$

On the assumption that small amounts of nitric oxide completely stop chain propagation, it is possible to calculate the chain length in the uninhibited reaction by the relation

$$\text{Chain length} = \frac{\text{Rate in absence of nitric oxide}}{\text{Rate in presence of nitric oxide}}$$

In the course of the reaction the nitric oxide is gradually consumed, but only very slowly. Thus, 2 mm. of nitric oxide can cut to about one-third the rate of decomposition of 400 mm. of ethyl ether, and yet last out the decomposition. The chain lengths found by this method in some typical cases are shown below:

CH_4 . . . . .4.7 at 850°C. and 100 mm.

C_2H_6 . . . . .17.8 at 600°C. and 100 mm.

C_6H_{14} . . . . .1.9 at 530°C. and 100 mm.

Echols and Pease (59, 60) have investigated the inhibition of the butane decomposition by this method. Their results indicate that the inhibitory effect is only transient, but that this is not due to the removal of nitric oxide by reaction. Thus, with 200 mm. of butane and 20 mm. of nitric oxide at 520°C., the initial rate of reaction is almost zero. At 20 per cent decomposition, however, the rate is back to normal, and only 10 per cent of the nitric oxide has reacted. They suggest that there is an equilibrium

$$R + NO \rightleftharpoons RNO$$
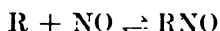
which is only slowly established.

Forsyth (82a) has investigated the effect of nitric oxide on the concentration of methyl radicals by the Paneth technique, using tellurium mirrors, and has obtained a value of 6.5 kcal. for the activation energy of the reaction $CH_3 + NO = ?$.

There is a considerable number of experiments which seem to indicate (287) that the maximum inhibition attained in the presence of nitric oxide does not correspond to complete suppression of chains, and hence that the chain lengths calculated by this method are too low. However, there appears to be no doubt that inhibition by nitric oxide is usually a reliable criterion for the presence of free radicals in a system containing a decomposing organic substance.

The nitric oxide inhibition method has also been used to detect radicals in the photolysis of mercury dimethyl (165, 322), azomethane (54), aldehydes (173a), and ketones (7a).

Taylor and Bender (307a) have recently investigated the pyrolysis of formaldoxime. They concluded that all the facts of nitric oxide inhibition can be explained on the assumption that a CH_3NO complex is initially formed and isomerizes into formaldoxime. The formaldoxime then decomposes and yields cyanides, ammonia, etc., which have been found by various workers in reactions inhibited by nitric oxide.

Methyl and ethyl nitrites have also been used to inhibit reactions in a similar way (241). In this case nitric oxide is produced *in situ* by the decomposition of the nitrites (243, 299, 300). Radicals are probably also removed by the reactions

$$R + R'CH \cdot ONO = RH + R'CHONO$$

and

$$R'CHONO = R'CHO + NO$$
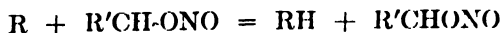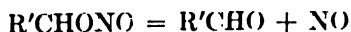
Rice and Polly have also shown (241) that a number of organic decompositions are inhibited by propylene. Inhibition of hydrocarbon decompositions also occurs in the presence (66, 67) of "isobutene" (methylpropene), 2,2,4-trimethylpentene, bivinyl, cyclohexene, and isoprene. Apparently the main requisite for inhibition in these cases is unsaturation, so that addition compounds may be formed with free radicals. It is well known that reactions of this type occur readily.

Oxygen has also been used as a detector for radicals and atoms. Locker and Patat added oxygen to formaldehyde in an investigation of its photolysis in order to detect free hydrogen atoms by reaction to form water (166, 198). Bates and Spence (13, 14) used oxygen similarly in the photolysis of alkyl halides. However, the possible reactions in these cases are too complicated for the method to yield reliable results.

(d) The detection of hydrogen atoms by reaction with solids

Hydrogen atoms have been detected by their reducing action on solids such as copper oxides, dyes, etc., by a number of workers (see, e.g., 28, 29, 46, 325). The method, however, is not suited to quantitative application. For a very full list of compounds which are reduced by atomic hydrogen see Glockler and Lind (101).

2. Spin-isomerism, isotopic labelling, etc.

(a) The para ortho hydrogen conversion

(1) *Determination of the hydrogen-atom concentration:* The equilibrium ratio of ortho- to para-hydrogen at temperatures from room temperature upwards is 3:1. At low temperatures, in the neighborhood of that of liquid hydrogen, the equilibrium corresponds to almost pure para-hydrogen, and by using charcoal as a catalyst for the conversion at low temperatures, para-hydrogen can thus be prepared. Para-hydrogen is stable at temperatures below *ca.* 500°C. for long periods, but the conversion to ortho-hydrogen at room temperature and up can be catalyzed by hydrogen atoms by the reaction

$$H + H_2 \text{ (para)} = H_2 \text{ (ortho)} + H$$
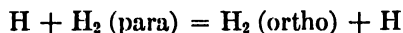
The kinetics of this reaction have been investigated by Geib and Harteck (94), using hydrogen atoms produced electrically, and by Farkas (70) with thermally produced atoms. The activation energy of the reaction is 6.7 kcal., with a steric factor of about 1/17 at room temperature, and of 1/7.5 at temperatures around 700°C.

Knowing the rate of the para–ortho conversion it is possible to calculate the hydrogen-atom concentration in a system which contains para-hydrogen by measuring the rate of the conversion. Thus, for example, Farkas and Sachsse (78) have determined the hydrogen-atom concentration in a system containing hydrogen and mercury, illuminated by the mercury resonance line, 2537 Å. Para-hydrogen was used in place of the ordinary equilibrium mixture. Samples

of hydrogen were withdrawn from time to time, and their para–ortho ratio was determined by measuring the thermal conductivity of the gas (71).

In simple systems the method is precise and yields unequivocal results (91). In more complex systems, however, difficulties are encountered in its application. In the first place the method cannot be used in a simple direct way unless the reaction by which the atoms normally disappear is considerably slower than the para–ortho conversion. Thus, the reaction

$$H + Cl_2 = HCl + Cl$$
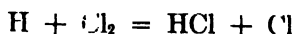
occurs roughly 10^4 times as fast as the para–ortho conversion catalyzed by hydrogen atoms at room temperature; hence it is only possible to determine the stationary hydrogen-atom concentration in the photochemical synthesis of hydrogen chloride by a special technique (278a).

A further difficulty is the fact that the para–ortho conversion is catalyzed by all paramagnetic substances, such as oxygen, nitric oxide, and substances containing an odd number of electrons, i.e., all free radicals. Hence in complex systems it is always difficult to ascertain if the conversion observed is due to hydrogen atoms or to other atoms or radicals.

In the case of deuterium the situation is reversed. The high-temperature equilibrium corresponds to a para-ortho ratio of 2:1, and nearly pure ortho-deuterium can be prepared at low temperatures. Obviously the same technique can be applied with deuterium, and the rate of conversion of ortho- to para-deuterium can be used as a measure of the deuterium-atom concentration (71, 73, 74).

In the investigation of exchange reactions involving atomic deuterium, it is sometimes possible to interpret the kinetics of reactions by using ortho-deuterium and another substance, and making simultaneous measurements of the rates of conversion and exchange. For example, Farkas and Melville (75) produced deuterium atoms by photosensitization in mixtures of ortho-deuterium and methane, and made simultaneous measurements of the rates of the reaction

$$D + CH_4 = CH_3D + H$$

and
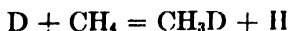
$$D + D_2 \text{ (ortho)} = D_2 \text{ (para)} + D$$
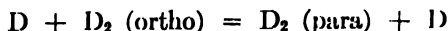
(2) Determination of radical concentrations: West (329) has made use of the fact that free radicals are paramagnetic, and should thus catalyze the para-ortho hydrogen conversion, to estimate radical concentrations. For example, methyl iodide was photolyzed in the presence of para-hydrogen, and it was found that the transitory products of the photolysis catalyzed the conversion. However, since atoms and other radicals also catalyze it, this cannot be regarded as a definite detection of the methyl radical (329a). West obtained similar results with acetone.

Rosenbaum and Hogness (256) found that the conversion was catalyzed by the products from decomposing hydrogen iodide. The rate was too fast to be

accounted for by catalysis by hydrogen atoms; hence it must have been catalyzed by iodine atoms as well.

Patat and Sachsse (199, 200, 202, 203, 258) have used an ingenious indirect method to measure radical concentrations and to test free-radical mechanisms by means of the para–ortho hydrogen conversion. For example, they measured the rate of the para–ortho hydrogen conversion in the presence of decomposing ethane, and were thus able to detect hydrogen atoms produced by the decomposition of ethane, or by the reaction

$$CH_3 + H_2 = CH_4 + H \tag{1}$$

They assumed that the direct catalysis of the conversion by methyl radicals is negligible compared with the effect due to hydrogen atoms. If we accept the Rice–Herzfeld mechanism for the ethane decomposition (236), the hydrogen atoms produced by equation 1 are being destroyed mainly by the reaction

$$H + C_2H_6 = C_2H_5 + H_2 \tag{2}$$
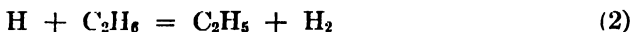
Hence the stationary concentration of hydrogen atoms is defined by the two processes, and we get approximately

$$\frac{(CH_3)}{(H)} = \frac{k_2(C_2H_6)}{k_1(H_2)}$$

Having evaluated the hydrogen-atom concentration, we can compare it with that calculated from the Rice–Herzfeld mechanism. At 590°C. the experimentally found value is 10^{-11} mole per liter. The value predicted by the mechanism is about 1000 times larger, viz., $10^{-8.2}$. This, therefore, appears to rule out the mechanism.

However, it is difficult to obtain unequivocal results by this method, since (a) the calculations depend strongly on the rate assumed for reaction 1, and are thus open to some question, and (b) the method can only yield results as to the truth or falsity of the Rice–Herzfeld mechanism in its detailed form, and depends completely on the activation energies assumed in this mechanism, especially for reaction 2 (see references 294, 295, and 296).

The method has been applied in a large number of cases by Patat and Sachsse, but it appears that its successful application demands a more detailed knowledge of the kinetics of the part reactions than is yet available in any given case.

(b) Exchange reactions

Just as the para–ortho hydrogen conversion

$$H + H_2 \text{ (para)} = H_2 \text{ (ortho)} + H$$

or

$$D + D_2 \text{ (ortho)} = D_2 \text{ (para)} + D$$
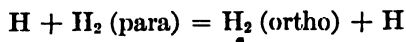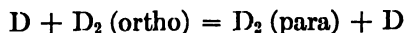
can be used as a measure of the stationary hydrogen- or deuterium-atom concentration in a system, so can the exchange reactions

$$H + D_2 = HD + D$$

and

$$D + H_2 = HD + H$$
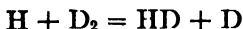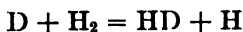
The kinetics of these reactions have been investigated by Farkas and Farkas (73). From their data the hydrogen- or deuterium-atom concentration in a system can thus be inferred from the rate of exchange. The extent to which the exchange has occurred can, like the para-ortho conversion, be inferred from thermal conductivity measurements.

An example of the use of this method is the investigation by Trenner, Morikawa, and Taylor (324) of exchange reactions of the paraffins by the Wood-Bonhoeffer method. In this work the deuterium-atom concentration in the system was determined by running hydrogen through the discharge, mixing the resulting H + H_2 with deuterium, and determining the extent to which the reaction

$$H + D_2 = HD + D$$
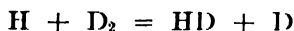
had occurred. The atom concentration was then calculated from Farkas and Farkas' results for this reaction, viz., $E = 6.55$ kcal., $k_{299} = 1.9 \times 10^5$ liter mole sec., $s = 0.1$.

In many cases isotopic exchange reactions can be used to cast light on certain elementary processes. Usually this is done by rather detailed considerations of mechanism. One especially simple phenomenon which can be investigated in this way is the following: Suppose that in a photolysis the primary step appears to be

$$RH = R + H$$
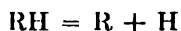
and that the quantum yield is low. It is desired to determine whether this is due to the back reaction proceeding efficiently, or to other causes. If deuterium is mixed with the reactant, then, owing to the reaction

$$H + D_2 = HD + D, \text{ etc.}$$

there will also be deuterium atoms in the system. Hence if the back reaction proceeds readily, in addition to

$$R + H = RH$$

the reaction

$$R + D = RD$$
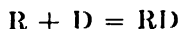
will also occur. By analyzing the "unreacted" reactant for deuterium it is therefore possible to determine if the reverse of the primary step is the cause of the low quantum yield. Examples of the use of this procedure are the reactions

$$NH_3 + h\nu = NH_2 + H \quad (313)$$

and

$$C_2H_6 + Hg(^3P_1) = C_2H_5 + H + Hg(^1S_0) \quad (285)$$
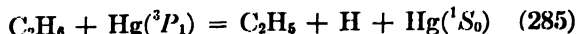
There are many other cases in which "tracer" experiments can thus shed light on primary processes. Not only deuterium, but also other isotopes, both stable and radioactive, have been used. A number of reviews of this type of work have appeared (92, 93, 226, 257).

3. Physical properties

(a) Diffusion

A fairly direct and reasonably accurate method of estimating the concentration of hydrogen atoms in a gas containing only H_2 and II has been devised by Wrede (340, 341) and Harteck (111). This can be used only at low pressures and for concentrations of atoms which are high enough to be of the same order of magnitude as that of the molecules. In practice, therefore, it is of use only with the discharge-tube method of producing hydrogen atoms.

In this method the stream of gas containing hydrogen atoms and molecules is led past a slit or capillary the width of which is smaller than the mean free path of the gas. For hydrogen at 1 mm. pressure this necessitates an opening with a width of about 1/20 mm. Under these circumstances atoms or molecules pass through the capillary only by diffusion. On the outside of the capillary there are then both atoms and molecules. Inside the capillary, however, owing to recombination on the glass surface, or on platinum or some other metal which may be placed there, there are only molecules. As a result, in the steady state the pressure will be lower on the inside than on the outside, since atoms diffuse faster than molecules in the ratio $\sqrt{2}$, but one molecule passing through the capillary transports twice the mass of hydrogen taken through by an atom. Hence, for 100 per cent atoms outside, we have

$$\frac{\text{Pressure outside}}{\text{Pressure inside}} = 2/\sqrt{2} = 1.41$$

Similarly, for a volume per cent, n, of atoms,

$$n = \frac{100(P_1 - P_2)}{P_1(1 - 0.5\sqrt{2})}$$

where P_1 is the pressure on the outside, and P_2 that on the inside.

The pressure measurements are usually made with a Pirani gauge, since McLeod gauges have so large a volume that a very long time is required for pressure equilibrium to be established on account of the smallness of the capillary. The use of as small a gauge as possible is important, since pressure fluctuations inevitably occur in a flowing system. To speed up pressure equilibrium Chadwell and Titani (47) used a sintered-glass disc instead of a single orifice.

The fact that foreign gases must be absent is a distinct handicap, since in investigating atomic reactions measurements of the atom concentration must be made in blank runs when other reactants are not present. The ideal case for the use of the method is in the investigation of the para-ortho hydrogen conversion, since in this case the above limitation does not exist.

While the method has occasionally been used for oxygen or nitrogen atoms, it is not very satisfactory since the mean free path at the same pressure is much smaller in these cases, and finer capillaries must therefore be used. As a result the establishment of equilibrium is extremely slow. In spite of these drawbacks it has been used successfully for chlorine by Rodebush and Klingelhofer (252).

Poole (217) has criticized all determinations with Wrede gauges on the ground that it is doubtful whether some mass-flow through the orifice has not occurred.

The method is inapplicable to free radicals, since systems containing them are always too complex.

(b) Calorimetry

Calorimetric methods of detecting and estimating hydrogen atoms have been frequently employed. The method is obviously attractive in principle, since the recombination of hydrogen atoms may be very easily brought about on catalyst surfaces, and the recombination is exothermic to the extent of approximately 103 kcal. per mole.

Calorimetric detection was first employed by Bonhoeffer (28), who coated thermometer bulbs with various substances and found that considerable temperature rises occurred. This method has also been used by Taylor and Lavin (315). Thermocouples have been employed in a similar way (213).

The use of glowing wires as a test for hydrogen atoms has been reported by Wood and by a number of later workers (see, e.g., 325). In this method the heat of recombination on a metal wire acting as a catalyst is sufficient to bring the wire to incandescence and thus afford a visual indication of the presence of atoms. One difficulty with this method is that the wire frequently becomes "poisoned." In one modification of the method (284) the wire is maintained at a just visible red heat (at which temperature poisoning does not occur) by the passage of a current. In the presence of atoms recombination heats the wire, and less current is necessary to maintain it at the same temperature. The decreased wattage is then a direct measure of the heat received from recombining atoms. The method is rough, but convenient.

More accurate calorimetric methods have been used by a number of workers (7, 25, 55. 276, 328). In all of these a catalyst mass is placed in the reaction tube at the place where the atom concentration is to be measured, and the heat received by the catalyst is measured by noting the temperature rise and applying cooling corrections, etc. The main difficulty is to correct for the loss by gaseous conduction, which is quite high and amounts to as much as 50 per cent of the observed temperature rise.

Objections to calorimetric methods have been raised on the grounds that the introduction of an efficient catalyst which causes complete removal of atoms sets up a diffusion of atoms towards the catalyst and thus alters the normal atom concentration throughout the reaction tube (7, 217, 301, 303, 328). However, it appears that with proper care in experimental arrangements this is not serious.

Poole (217) has recently described a continuous-flow calorimeter which seems to meet the objections which have been raised to the method, and which greatly cuts down conduction losses.

Schwab and Friess (267) have used the heating of a copper-constantan thermocouple as a method of determining chlorine atoms. This was used only for relative measurements. For absolute measurements they used a calorimeter consisting of a thin metal plate in which a thermocouple was imbedded. This

was heated by atom recombination, and was calibrated by heating electrically in blank experiments.

Schwab (264) has also used the heating of a thermocouple to measure the relative concentration of bromine atoms produced by the discharge-tube method.

There are indications that heating of a wire by recombination may have uccessfully indicated the presence of hydroxyl radicals (325).

(c) Thermal conductivity

Senftleben and Germer (268) detected chlorine atoms in chlorine illuminated with light in the region of the continuum by means of the increased thermal conductivity of the gas. Senftleben and Riechemeier (268a) in a similar way have measured the stationary hydrogen-atom concentration in mercury–hydrogen mixtures illuminated with λ 2537.

(d) Pressure change

In a few cases the increase in pressure on dissociation of a molecule into atoms (or the decrease on their recombination) has been used as a qualitative or quantitative indication of the presence of atoms. Thus, by a special technique Smallwood (277) was able to compress very quickly a mixture of hydrogen molecules and atoms from a discharge, and to follow the recombination process by measuring the pressure with a diaphragm gauge with photographic recording.

In the case of chlorine and bromine, the well-known Budde effect (38) indicates the production of atoms by the rise in pressure obtained when photochemically produced chlorine atoms recombine and give out heat.

(e) Mass spectrograph

Early attempts to use the mass spectrograph as an analytical tool (187a) were complicated by the electron dissociation of the parent molecule, but Eltenton (60a) has recently taken advantage of the fact that the ionization potentials of free radicals are lower than the appearance potentials of the same ions produced by electron dissociation. In contrast to the results of Belchetz and Rideal, he found methyl radicals but no methylene radicals in the decomposition of methane. He was also able to detect methyl and ethyl radicals in the decomposition of ethane, methylene from diazomethane, and allyl radicals in the reaction of methyl radicals with propylene.

4. Optical methods

(a) Emission spectra

"Emission spectra cannot serve as a quantitative measure of the concentration of free radicals since, for the appearance of an emission spectrum, not only the occurrence of free radicals but also their excitation is necessary" (126). The same remarks obviously apply to atoms as well. Even from a qualitative point of view, emission spectra cannot in general be used as an indication of the presence of atoms or radicals, except in a few special cases (see below) or where

high energies are involved (as in discharges, flames, or in photochemistry of the Schumann region), so that any radicals formed are in excited states and thus emit radiation.

In discharges, etc., a large number of radicals have been detected, such as C_2, CH, CN, NH, OH, PH, and ions of various sorts. (For reviews of this subject see references 26, 101, 126, and 280.) In flames and explosions C_2, CH, OH, NH, and probably CHO and other radicals have been observed (32, 89a, 93a, 98a, 132, 134, 163, 323, 325a). In the Schumann region a considerable number of atoms and radicals have been detected in emission during photolyses (see, for example, references 182, 220, 342).

Resonance emission has been used in a number of cases to detect and measure the concentration of atoms and of unstable molecules. Hartel and Polanyi (120) followed the changes in the concentration of sodium atoms in reaction mixtures by illuminating with sodium resonance radiation (the D line) and measuring the intensity of the resonance radiation emitted.

In a qualitative way the presence of HgH in mercury–hydrogen mixtures illuminated with λ 2537 (23) and of CdH and ZnH in the corresponding experiments with cadmium and zinc (19, 187) has been established by the resonance emission of HgH, CdH, and ZnH bands. It should be noted that the successful detection of atoms or radicals by the resonance emission of lines or bands originating on the ground state depends on the atoms or radicals being in the ground state rather than in excited states.

Bay and Steiner (11) have used emission spectra to measure atom concentrations in a Wood's tube. A pair of subsidiary electrodes were placed in the reaction tube, and a weak high-frequency discharge was passed between them. By observing this spectrographically and determining the ratio of the intensities of certain atomic lines to molecular bands, it was possible to use the method as a relative measure of the atom concentration. Or, by running calibration experiments against a Wrede gauge, the spectroscopic observations could be made to give absolute values of atom concentrations.

(b) Absorption spectra

In principle the detection and estimation of atoms and radicals in absorption is without difficulty. In practice, however, it is necessary that the concentration be fairly high for this method to be successful. (See reference 186 for a discussion of the difficulties involved.)

Bonhoeffer and Reichardt (37) photographed the hydroxyl bands in absorption in a flow system with steam at temperatures in the neighborhood of 1600°C., and were thus able to determine the equilibrium in the reaction

$$H_2O = H + OH$$

Bonhoeffer and Pearson, however, were unable to find the hydroxyl radical in absorption in the gas flowing from a discharge through water vapor (36). Geib and Harteck (113) were also unable to find it spectroscopically in the reaction of hydrogen atoms with oxygen.

Oldenberg (87, 184, 185, 304), by using a 21-ft. grating, found the hydroxyl radical in absorption in a discharge in water vapor.   He was able to detect it for as long as 1/8 sec. after the discharge was interrupted.

The hydroxyl radical has frequently been found in absorption in hydrogen and hydrocarbon flames (9, 33, 134, 144, 145, 146, 147, 148, 163).

Franck and Reichardt (83) detected the NH radical in absorption in a flow system in decomposing ammonia at 2000°C.

Kistiakowsky and Gershinowitz (139, 140) and White (332a) investigated the dissociation of cyanogen,

$$(CN)_2 = 2CN$$
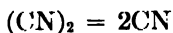
in the neighborhood of 1200°C. by using absorption spectroscopy with a flow system.

The C_2 radical was detected in absorption by means of the Swan bands in the reaction

$$C_3O_2 = CO_2 + C_2$$

by Klemenc, Wechsberg, and Wagner (142).

For a review of the detection of CH and other radicals in absorption see Willey (333).

Rabinowitsch and his coworkers (221, 222, 223) have measured the atom concentration in illuminated systems containing the halogens by measuring the extinction coefficients, and from these calculating the decrease in the number of molecules present, and hence indirectly the atom concentration.

Hydrogen-atom concentrations have also been measured by absorption (217a).

(c) Miscellaneous optical methods

Kohanenko (143) has detected radicals and atoms by means of a glowing screen of zinc sulfide, as described previously.

In investigating the reaction between mercury vapor and the halogens, Ogg, Martin, and Leighton (183) used light from a resonance lamp to cast a shadow of a mercury-vapor jet, and thus followed the decrease in concentration of the mercury vapor by a method analogous to the diffusion flame technique.   In this way they were able to follow relatively fast reactions with activation energies of the order of 5 kcal.

Kudrjawzewa and Prileshajewa (149) used an ingenious method to investigate the photodecomposition of adsorbed acetone.   The acetone was adsorbed on a thin metallic mirror, and a spectrum was focussed on it.   The photochemically effective light formed radicals which removed the mirror at the part of the spectrum which was effective.   In this way the photochemical threshold for adsorbed acetone was determined.

5. Inference

In practice the presence of radicals, their concentration, etc., is often arrived at by inference from investigations conducted by ordinary methods.   Thus the

mechanism of a reaction may be arrived at, sometimes with considerable certainty, by conclusions based on rates of formation of stable products as determined by pressure change, analysis, etc., and by the effect of temperature, pressure, etc. on these rates. If a mechanism can be established by such means, radical concentrations and the rates of elementary reactions can then be calculated. This is frequently a very useful method, although it can hardly be classed as an investigation of the elementary processes in question.

Another method of arriving at the activation energies of elementary reactions which is frequently employed makes use of the fact that the heat of the reaction is equal to the difference between the activation energies of the forward and the reverse reactions. The heat of the reaction can, in turn, be calculated from a knowledge of the strengths of the bonds formed and broken in the reaction. Hence if we know the activation energy of a reaction and the strengths of the bonds involved, we can estimate the activation energy of the reverse process. The difficulty is that there is usually no very certain knowledge of the bond strengths.

III. SUMMARY OF METHODS

In conclusion it may be well to summarize the main methods of investigation discussed above, from the point of view of reliability, errors, etc.

A. THERMAL DECOMPOSITION—STATIC OR FLOW METHODS

From such investigations valuable information is usually obtained. However, from a radical or atom point of view all information is obtained strictly by inference, and is thus correspondingly uncertain.

B. THERMALLY SENSITIZED DECOMPOSITIONS

This type of investigation gives very definite information whether or not radicals react with a substance under certain defined conditions, and whether free-radical chains are set up. However, the results are usually quite indefinite as to what the reaction is between the radicals and the substrate.

C. INHIBITION

This gives definite information regarding the occurrence or non-occurrence of free-radical chains in the decomposition. It gives rather dubious information about the lengths of such chains. It gives, however, no information about the nature of the reactions involved.

D. THE PANETH—RICE METHOD

This is much the most direct method in so far as the detection and identification of radicals are concerned. However, this detection is difficult, and in certain cases, notably methylene *versus* methyl, the results are equivocal. The method furnishes reliable values of the activation energies of the split of stable molecules into radicals at high temperatures. It is not, however, well adapted to the determination of the rates or activation energies of other types of radical reactions.

E. THE BELCHETZ–RIDEAL TECHNIQUE

This appears to have definite merit as far as the detection of *primary* products is concerned. However, the present status of work done by this method is somewhat uncertain, and a reinvestigation would be of decided value.

F. DILUTE FLAMES AND DIFFUSION FLAMES

The main advantage of these methods is their applicability to very fast reactions. They appear to be among the most reliable methods as far as atomic reactions are concerned. The extension of the methods to free radicals produces such complex systems that the results obtained are rather indirect, and are much less certain.

G. PARA–ORTHO HYDROGEN CONVERSION

The use of this method to determine the hydrogen-atom concentration in simple systems undoubtedly gives reliable results. In more complex systems it is impossible to decide to what extent the conversion obtained is due to other paramagnetic substances. The Sachsse–Patat modification of the method is too dependent on a detailed knowledge of the mechanism of the processes which are occurring to be of much value.

H. THE WOOD–BONHOEFFER METHOD

As a means of producing atoms, this is the best of all methods, since a definite high concentration results. The further reaction steps are arrived at by inference from the final products, and are thus on much less certain ground. Surface effects are also a source of considerable uncertainty. A combination of this method with the Paneth -Rice technique appears to offer interesting possibilities.

I. PHOTOLYSIS

The results of photolytic experiments suffer from the same uncertainties as those of thermal reactions, since a detailed mechanism must be established from a consideration of the final stable products of the reaction and their variation with pressure, temperature, light intensity, etc. The rates of elementary reactions are then deduced from this mechanism. However, there is one distinct advantage over thermal reactions: namely, that the primary step may be definitely established from spectroscopic data.

J. THE PEARSON TECHNIQUE

This gives very definite information as to the *presence* of radicals in photo-decompositions. The identification is often definite, but is difficult, since the quantities of material to the analyzed are in general even smaller than with the ordinary Paneth method. The method is only suitable for the detection and identification of the primary products of photolyses.

K. SENSITIZATION BY RADICALS PRODUCED BY PHOTOLYSIS

This method, especially in the form employed by Taylor and his collaborators, gives very direct information concerning the rates of reaction of radicals with molecules. The main difficulty is the possibility that, for example, in a reaction

$$CH_3 + HX = CH_4 + X$$
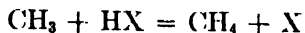
methane may be formed by reactions other than the one being investigated.

L. PHOTOSENSITIZATION BY METAL VAPORS

This is a very useful method of producing hydrogen atoms. As compared with the Wood–Bonhoeffer method, however, it is much more difficult to determine the stationary hydrogen-atom concentration.

In the case of other reactions the difficulty is that, as with photolysis, a mechanism must first be established by inference, and the rates of elementary reactions then deduced from such a mechanism. The primary step is not as easy to establish as in photolytic experiments, but it can usually be well established if sufficient quenching information is available.

M. EXCHANGE REACTIONS

These give much useful information. This is not a real "method," however, since it must always be combined with one of the foregoing.

Difficulties and uncertainties

It may be said that no single investigation of an elementary reaction has ever been made which is free from ambiguity. The only possible procedure is the accumulation of data, and the testing of mechanisms by consideration of their compatibility with results obtained by various experimental methods. In conclusion it may again be pointed out that the activation energies of elementary reactions are never *measured*, but are calculated from the temperature coefficients of processes the nature of which must be arrived at by indirect means.

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PARTICLE-SIZE STUDIES

PROPERTIES OF FINELY DIVIDED MATERIALS

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A survey of the literature on particle-size studies indicated the desirability of classifying particle properties according to their influence on other properties. Such a classification was made, and experimental data were discussed on the basis of this classification. A study of five closely fractionated materials, having different particle shapes and about 50 microns in size, was made in which it was shown that the two mean microscopic diameters based on the square root of the projected area and the shorter of the two visible dimensions at right angles to each other gave results essentially the same for silica, coal, slate, and galena, while for mica the latter microscopic diameter gave results equal to 0.9 of the former. The mean microscopic diameter was found to vary from 1.2 to 1.5 times the sieve aperture and from 1.1 to 2 times the equivalent sedimentation diameter, depending upon the material. The mean sedimentation diameter of materials just passing a sieve may be from 0.8 to 1.2 times the sieve aperture, but the point of separation of a No. 325 sieve for combined sieving and sedimentation analyses may be taken as 53 microns for many materials. It was pointed out that the computation of specific surface from size-distribution data, using shape constant ratios, rather than from surface and volume constants would simplify the problem considerably.

Particle-size studies in the range of sizes from the finer sieve sizes of about 75 microns down to about 0.2 micron are of increasing industrial value because the variations in particle properties affect the production and use of such materials. (The colloidal range which is predominantly finer than 0.2 micron, although approaching this size as an upper limit, is not included in the scope of this work.) Although there have been many publications on certain specific properties of particles (such as size or shape), the results have never been assembled and studied in relation to other particle properties. The object of this paper was to review the more important studies and to classify particle properties according to their influence on other properties. Certain experimental data were then studied on the basis of this classification.

A single particle may be evaluated in terms of three primary functions: dimension (or size), dimensional relationships (or shape), and surface configuration (or structure). If a material consists of more than one particle and a range of sizes, the additional primary property of size distribution must be considered. These primary properties control the secondary properties, such as specific surface, the packing characteristics, flocculation in suspensions, obscuring power to radiations, and chemical activity. In the following classification certain of the above properties have been discussed on the basis of experimental results for different types of materials.

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I. Primary Properties

A. PARTICLE SIZE

1. Microscopic diameters

Observation of finely ground particles under the microscope shows the necessity of defining particle size by some arbitrary diametric dimension, since very few materials are spherical in shape. Among the most important diameters that are used to define the size of particles of irregular shape are the following: (a) the diameter of Green (23, 24), which is a statistical diameter, d_g, taken in one direction across the particles lying on the same line across the field; (b) the diameter of Heywood (26, 27, 28), which is the diameter, d_h, of a circle having the same projected area as the particle; (c) the diameter of Wadell (48), who uses a true nominal diameter, d_n, which is the diameter of a sphere having the same volume as that of the particle; (d) the diameter of Martin (34), which is similar to that of Green except that the diameter, d_m, is that which divides the projected area of the particle into two equal areas; (e) the diameter of Perrott and Kinney (36), in which the diameter, d_k, is the side of a square having the same area as the projected area of the particle; (f) the diameter of Weigel (52), which is the visual average, d_w, of the two visible dimensions; (g) the diameter of Work (55), who used a diameter, d_b, which is the "intermediate" dimension, being the shorter of the two visible dimensions at right angles to each other; (h) the diameter of the preceding author, who suggested a mean spherical diameter, d_v, which is the diameter of a sphere having the average weight of the particles; (i) the diameter of Andreasen (2), which is the cube root, d_a, of the volume of the particle. Other diameters that have been used are: (j) a harmonic mean diameter, d_e, which is equal to three times the reciprocal of the sum of the reciprocals of the three individual dimensions (length, width, and thickness); (k) a diameter, d_c, equal to the cube root of the product of the three dimensions; and (l) a diameter, d_r, equal to the arithmetic average of the three dimensions at right angles to each other.

Perrott and Kinney (36), using coal, have shown a comparison of various types of microscopic diameters computed to weight distribution. These authors have also compared results obtained using their diameter (d_k) with those obtained by water sedimentation and air elutriation; for the 0–7.5 micron fraction the last two methods agree, but the microscope gives low results. They also showed that, for coal, d_c is essentially equal to d_r and both do not vary greatly from d_k. They showed further that the weight calculated from nd^3 is about 1.5 times the actual weight but varies from 1.4 to 1.8 times as much. This would be expected, since the volume of a cube is $(6/\pi) = 1.92$ times as great as that of a sphere the diameter of which is equal to one edge of a cube; this is also the ratio of surface. The ratio becomes less as the particle approaches a sphere in shape and all three dimensions are averaged.

Weigel (52) has used d_w for studies on various types of mineral fillers and has given a comparison of sizes by count with results on settling velocity. This author computed the mean diameter of the material from $\Sigma nd^3/\Sigma nd^2$ (where n

is the number of particles of diameter d) and for talcs, micas, and slates applied a percentage correction to the diameter. Heywood (28) has shown that d_a/d_k may vary from 1.3 for rounded sand to 7.0 for mica in coarse sizes. A comparison of d_L and d_k shows that the calculated ratio of d_k/d_L is equal to
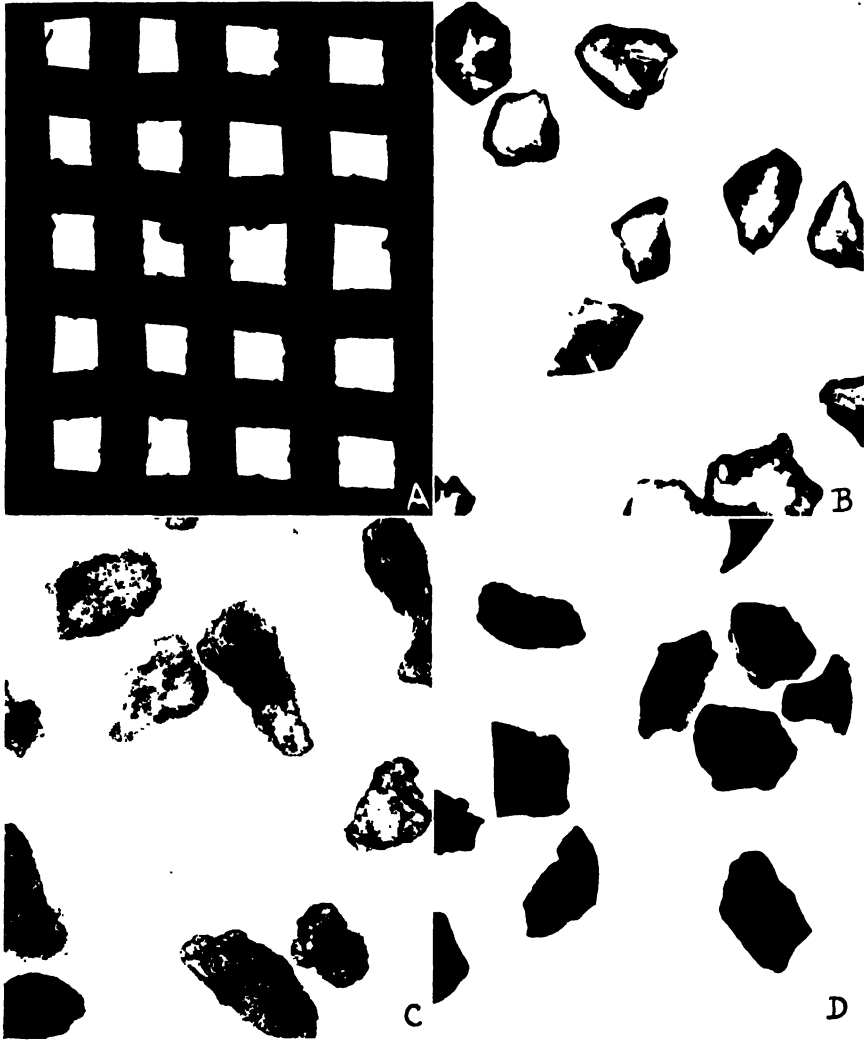
FIG. 1. Photomicrographs: A, No. 325 sieve; B, silica; C, slate; D, coal; E, galena; F, mica; G, scale, one division equals 10 microns; H, diatomaceous earth.

$(2/\sqrt{\pi}) = 1.13$. Patterson and Cawood (35) have described a graticule for oculars containing etched circles which might be useful in measuring d_k. Work (55) has shown d_r to be from 0.9 to 1.0 times the sieve aperture for large sizes. Bennett (7) has shown an equivalent "projected diameter" to be 1.4 times the sieve aperture of square sieves and 1.21 times the aperture of round holes, "as

suggested by Heywood." Roller has stated that the ratio of d_t/d_c is generally less than 1.06 and that the arithmetic mean may therefore be used in place of d_c. Gadd (20) has stated that d_m is about the same as d_t. Weinig (53) has proposed a method of computing surface based on a comparison of the particle with a
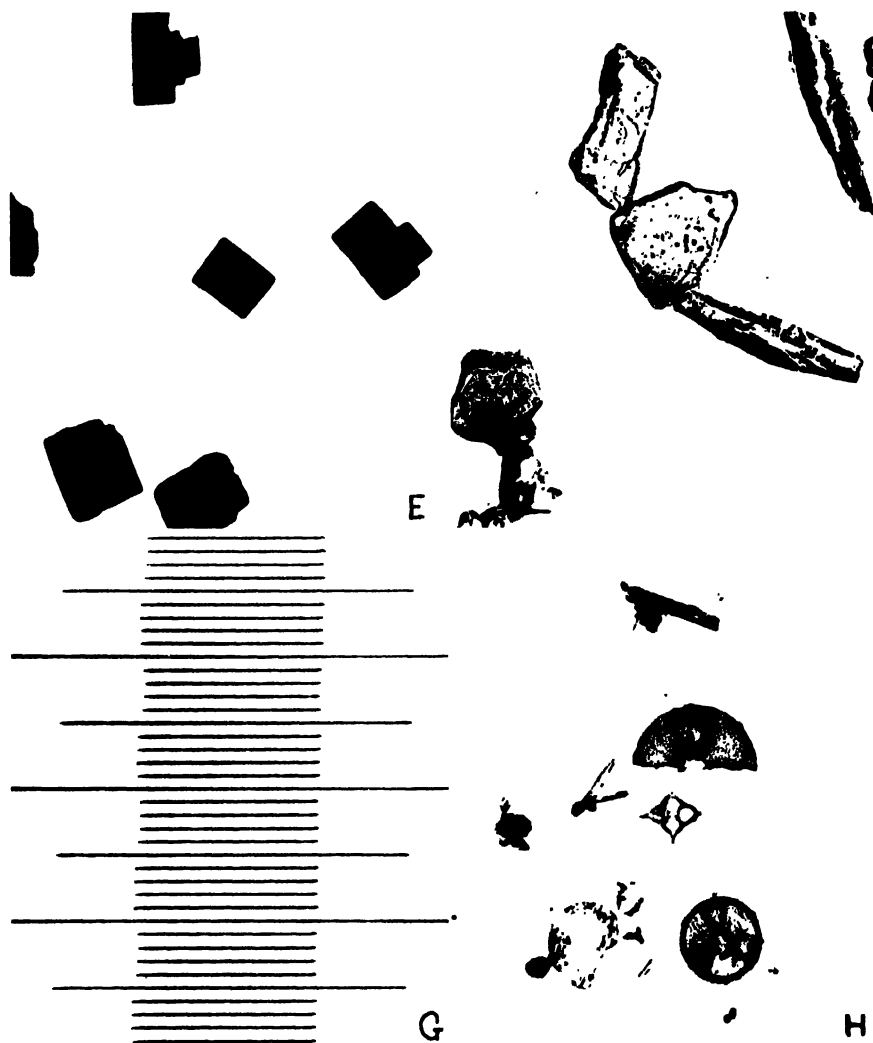
F1G. 1-concluded

cubical configuration. These shape constants approach a constant value in the No. 65 to No. 100 sieve range and are similar for different types of crushing operations.

The preceding review of the literature indicates the numerous ways in which microscopic dimensions may be reported. Results of different investigators

cannot be compared unless the relations among the various diameters are known, and few are. Microscopic analysis is, at best, a laborious and time-consuming operation, and it seems pertinent to suggest that standard procedures be used. The most simple microscopic diameters to determine are those of Perrott and Kinney (d_k) and of Work (d_b). Experience with the former has indicated its general adaptability, but the latter is somewhat more rapid to use. For this reason the following experiments were carried out to ascertain the relations between the two. Five materials representing particle shapes frequently encountered in practice were selected and subjected to the following operations to obtain uniform fractions. Fifty to 100 g. of finely ground powder were weighed and sieved through a No. 325 sieve, using a water-spray nozzle (4) at 10 pounds per square inch pressure for 10 min. The residues were dried and weighed and
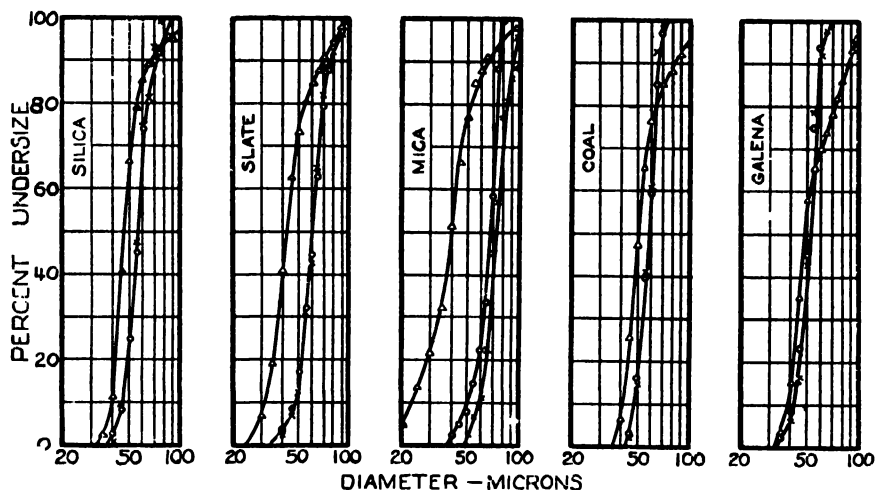
Fig. 2. Size distribution curves: ×, d_k; ○, d_b; △, turbidity

then placed on a new No. 325 sieve and sieved dry for 5 min., using a mechanical shaker of the vibratory type. The material passing was recovered and used for study. It consisted of a closely fractionated product that would pass a No. 325 sieve dry but not when sieved wet.

The above procedure was used for the following different materials: a ball-mill-ground Ottawa sand, D-2; a ring-roller-mill-ground green slate, 470; a green mica, 432, method of processing not known; and ball-mill-ground samples of coal, C, and galena, G. These five materials cover particle shapes representative of the acicular (slate), angular (coal), platelike (mica), regular cubical (galena), and angular to rhombohedral (silica) types of particles. The characteristic shapes of these materials are illustrated in figure 1. Figure 1A is a photomicrograph of a portion of the sieve used for dry sieving. Figure 1H is a photomicrograph of diatomaceous earth retained on a No. 325 sieve, using the wet sieving procedure.

TABLE 1

Comparison of data on 325-mesh material and certain other materials

MATERIAL	NO.	D_s IN GRAMS PER CUBIC CENTI- METER	PER CENT PASSING A No. 325 SIEVE		325-MESH MATERIAL	MEAN DIAMETER*					SPECIFIC SURFACE† IN SQUARE CENTIMETERS PER GRAM			
			(a)	(b)	(c)	d_k (e)	d_b (e)	d_s (f)	d_t (g)	d_h	S_k	S_b	S_s	S_t (i)
Silica..........	D-2	2.67	78.8	77.8	1.87	57	58	48	48	58	$66K$	$65K$	$78K$	$79K$
Green slate....	470	2.82	96.4	93.8	2.50‡	62	62	38	42	58	$57K$	$57K$	$93K$	$85K$
Green mica....	432	2.92	82.5	80.7	0.52	73	66	35	35	27	$47K$	$52K$	$99K$	$99K$
Coal........	C	1.75	73.4	64.1	4.84	59	59	50	52	50	$97K$	$97K$	$114K$	$111K$
Galena........	G	7.66	65.3	57.6	7.26‡	52	52	48	50		$27K$	$27K$	$29K$	$26K$
Red slate.. ..	642	2.80	96.4							47				
Silica.... ...	196	2.62	94.8							50				
Silica.	W-1	2.67	29.7			62§				51				
Silica.... ...	F-14	2.67	98.0			58§				58				
Traprock... ..	113	2.91	83.4							51				

* Diameters:
  d_k = diameter based on square root of projected area,
  d_b = diameter based on shorter of two visible dimensions at right angles to each other,
  d_s = diameter based on sedimentation,
  d_t = diameter based on turbidity data, and
  d_h = diameter read from sedimentation curves of whole powder at per cent undersize found under (a).
† The subscripts under specific surface refer to the corresponding surface mean diameter.
K is the shape constant ratio which may vary for different materials.
Column headings:
  (a) Sieve test: 1-g. sample on 2-in. sieve with 10 lb. per square inch nozzle pressure for 1 min.
  (b) Sieve test: 50-g. sample on 8-in. sieve with 10 lb. per square inch nozzle pressure for 10 min.
  (c) Per cent passing a No. 325 sieve dry but retained wet; 50-g. sample.
  (e) Calculated from $\Sigma nd^3/\Sigma nd^2$.
  (f) From midpoint of sedimentation curve in region of greatest slope.
  (g) Calculated from turbidity specific surface.
  (i) From turbidity data, obtained by dividing the specific surface obtained by 6; the latter is the shape constant ratio which is assumed in this method.
‡ 100-g. sample.
§ Read from microscopic count of whole powder at per cent undersize found under (a).

TABLE 2

Comparison of various particle diameters for different materials

MATERIAL	$d_b/44$	d_s/d_b	$d_s/44$
Silica, D-2...............................	1.32	0.83	1.09
Slate, 470................................	1.41	0.62	0.87
Mica, 432................................	1.50	0.53	0.80
Coal, C..................................	1.34	0.85	1.09
Galena, G...............................	1.18	0.92	1.14

A microscopic count at 5-micron intervals was made, using five fields from each of two slides to give a minimum of one hundred particles counted. From these data a weight distribution for the Work diameter, d_b, and the Perrott and Kinney diameter, d_k, could be computed as well as the surface mean diameter. The weight distribution was calculated from $nd^3/\Sigma nd^3$ and the surface mean diameter from $\Sigma nd^3/\Sigma nd^2$, where n was the number of particles of diameter d. The weight distributions are shown in figure 2 and the mean diameters are given in table 1.

Study of the data shows, with the exception of the mica, that the diameter of Work, d_b, and that of Perrott and Kinney, d_k, give essentially the same values both for distribution and for surface mean diameter. In the case of the mica the ratio of d_b/d_k is about 0.9.

The data for these materials also show (table 2) that the d_b diameter of the particles just passing a No. 325 sieve (nominal opening of 44 microns) may be from 1.18 to 1.50 times as great as the aperture.

2. Sedimentation diameter

With the exception of sieve analysis and microscopic methods, practically all of the methods used for determining particle-size distribution define the size in terms of the sedimentation diameter. This is the diameter of a sphere that settles at the same velocity as the particle being studied.

In general, isothermal free settling of particles may be assumed to follow this form of Stokes' Law:

$$d = \sqrt{\frac{18\eta v \times 10^8}{(D_s - D_1)g}} \tag{1}$$

where η = viscosity, in poises,

v = terminal velocity, h/t,

h = distance of fall, in centimeters,

t = time of fall, in seconds,

g = gravitational constant in centimeters per second per second,

D_s = density of particle (greater than D_l), in grams per cubic centimeter,

D_t = density of liquid, in grams per cubic centimeter, and

d = diameter of a sphere in microns.

For irregular shaped particles, d is the diameter of a sphere that falls at the same rate as the particle. This equation is valid for Reynolds numbers below 1 where the Reynolds number is defined (51) as:

$$Re = \frac{vdD_s}{\eta \times 10,000} \tag{2}$$

While numerous studies on Stokes' Law have been published, there are few on the application of it to the practical problem of relating settling velocity and the diameter of subsieve particles of irregular shape. These relations are of importance where the conversion of particle-size data is required, as, for example, in the computation of the surface area of a powder from its weight distribution.

The analysis of the settling of particles generally takes the form of a plot of a modified Reynolds number against a coefficient of resistance with parameters for variation in shape. Wadell (49) has developed such curves for the "true nominal diameter," which is the diameter of a sphere having the same volume as that of the particle. In another article by this author (50) it is indicated that equivalent diameter (Stokes' Law) and true nominal diameter are nearly the same at low Reynolds numbers. Methods are given for computing equivalent diameters and equivalent velocities by combining equations to eliminate diameter or velocity, as the case may be.

Recent papers on the validity of Stokes' Law are those of Dorr and Roberts (15), who showed its limit to be at about Reynolds numbers of 1 and gave a modified equation for higher Reynolds numbers, and that of Squires and Squires (41), who showed that the settling of thin discs may vary, depending upon the orientation of the particle relative to the direction of motion. They stated, further, that discs and spheres settle at the same velocity only when the ratio of the diameter of the disc to its thickness is 1.77 for discs settling with face perpendicular to the direction of motion; in this respect they disagree with Wadell (50). Svedberg (43) has published a table showing calculated relative velocities for disc- and rod-shaped ellipsoid particles for various axes ratios; the values showed a variation of from about 0.75 to 1.0 times the velocity of fall for spheres. He also mentioned the wall effect for settling, with an indicated correction of 1 per cent for particles 0.01 of the distance between the enclosing walls. The wall effect has also been discussed by Squires and Squires (41) and by Wadell (50). Marshall (33) has discussed orientation and shape effects in settling and has stated that shape can be neglected for length-to-thickness ratios of 5 to 1 only if the volume of the particle is twice that of spheres. On the basis of shape factors, Heywood (27) has proposed a method for correcting equivalent diameters and equivalent velocities by means of plots of true Reynolds numbers *versus* Stokes-Reynolds numbers.

Since many of the methods described later have been used to measure the particle size of emulsions, it is desirable to know how liquids follow Stokes' Law. Bond and Newton (9) have shown theoretically and experimentally that surface tension is a factor to be considered in certain size ranges. Previously, Bond (8) had indicated that the terminal velocity of spherical drops or bubbles may be up 1.5 times that of solid spheres of the same shape and mass.

The preceding review of studies on the settling velocity of irregularly shaped particles of ideal configuration suggested a similar study on ground materials of various shapes. For this purpose the same five fractions were used on which the microsopic counts had been made. A sedimentation analysis was made by means of the Wagner turbidimeter (4), and a plot of the diameter (calculated from Stokes' Law) against the fractional transmission was drawn. From this plot, shown in figure 3, the mean sedimentation diameter was obtained by interpolation of the midpoint of the curve in the region of steep slope. The mean diameters are given in table 1, and a comparison of d_s and d_b is shown in table 2. The data indicate that the sedimentation diameter may be from 0.5 to 0.9 the

microscopic dimension and that the difference in the two diameters is less where the several dimensions of the individual particles are similar in magnitude.

The variation in the ratio of d_s/d_b explains the discrepancies noted in the literature where size distributions based on sedimentation methods are compared with microscopic counts. It is obvious that such comparisons cannot be made
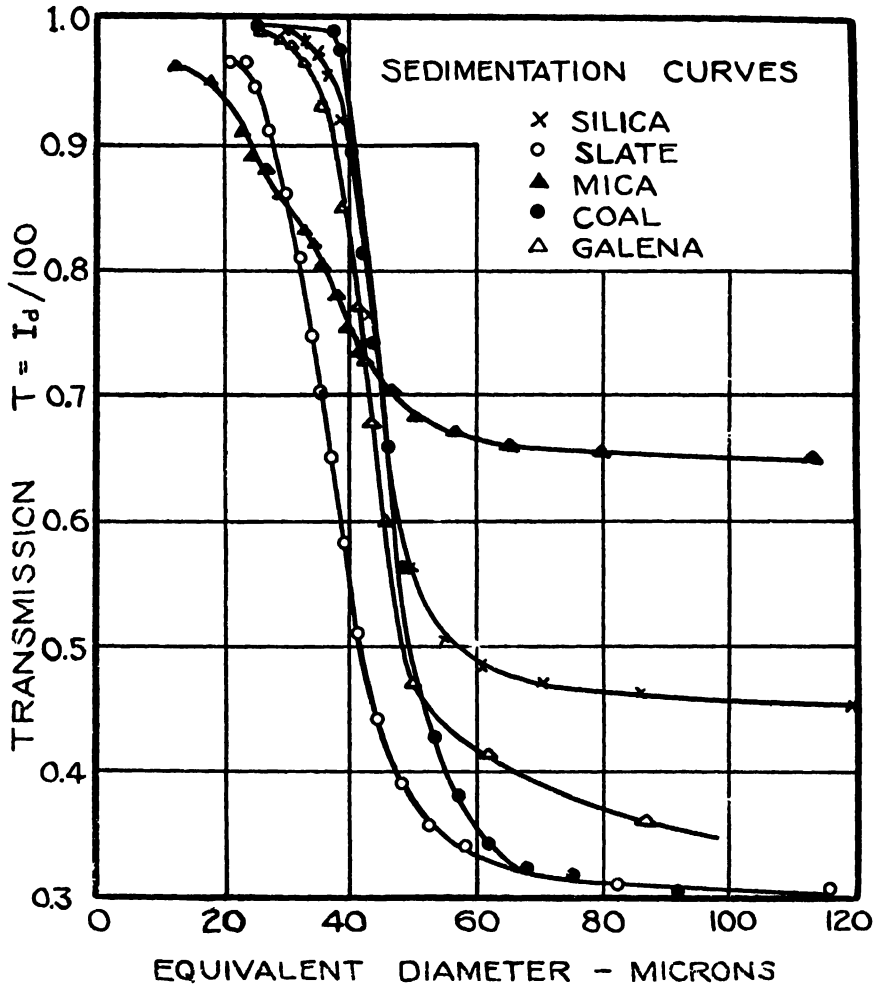
Fig 3. Sedimentation curves

unless corrections are applied to one or the other diameters. In the case of mica the low ratio is a result of the effect discussed by Squires and Squires (41), who showed that the sedimentation velocity of thin discs when oriented vertically is 57 per cent greater than when oriented horizontally. Actually, a random orientation probably exists for platelike particles, giving a measure of particle-size distribution that is a "statistical" measure when sedimentation methods are used for such materials.

From a practical viewpoint the relation of settling diameter to sieve aperture is very important. Fritts (19) has shown that for a certain cement the diameter of spheres having the same velocity of settling as the particles passing a No. 325 sieve is 45 microns. A recent communication from him has indicated that for other cements the diameter of the sphere is more nearly 1.21 times the sieve aperture which is the mean of the diameter of the circumscribing circle and that of the circle inscribed within a square aperture. Other investigators have indicated a similar relation for different types of materials. The results for the five materials used in this study are given in table 2 and indicate some variation. The particle diameter may be either greater or smaller than the sieve aperture, depending upon the material. The relative settling velocities of the platy and acicular particles are smaller than for regularly shaped particles of the same diametric dimension, and, in addition, the settling diameter is smaller than the sieve aperture.

However, the size passing a No. 325 sieve from sedimentation analysis of the whole powders from which these fractions were obtained does not show the wide variations just discussed. If the size at the per cent passing a No. 325 sieve (corresponding to the amount obtained on the standard 1-g. wet test) is read from the cumulative per cent curve obtained by sedimentation analysis, it is found that the diameter is approximately the same within the limits of experimental error for most materials, as shown in table 1 under the d_h column. The distribution curves of the whole powders were averaged results from sedimentation analyses by pipet, hydrometer, and/or air elutriation. The value for d_h would be expected to be larger than d_s for the fractions discussed previously, since d_h in reality measures the upper limit of the particles just passing the sieve. The fact that d_h is approximately the same for different materials has a definite practical application where the particle-size distribution is such that both sieve analysis and subsieve methods must be used. An arithmetic average of all figures (except for mica) gives a value of 53 microns, which can be used as the point of separation for the No. 325 sieve where combined sieving and sedimentation methods are used. The data for mica are abnormal, as might be expected, since sieve analysis of platelike materials gives erratic results. This is true because the plates lie with their flat sides on the sieve, thereby tending to reduce the aperture.

The mean value of 53 microns is 1.21 times the sieve aperture, which is in accord with the results of Andreasen (3). In that study it was found (for flint particles only) that if the sedimentation diameter were multiplied by 0.806 (the ratio of the edge of a cube to the diameter of a sphere of the same volume), the sedimentation data would agree with sieve data. Thus, the sedimentation diameter was 1.22 times the sieve opening. This ratio (0.806), however, must not be inferred to apply in the conversion of sedimentation diameters to microscopic dimensions, since the latter are larger than the former, as has been discussed. It should be noted that in using these corrections for combined sieve and sedimentation analysis, it is more expedient to correct the sieve dimensions to equivalent sedimentation diameters than the reverse, because most calcula-

tions in practice are based on subsieve data, which are determined for the most part by sedimentation methods.

B. PARTICLE SHAPE

While there have been many published articles on the measurement of the properties of particles wherein the particles are assumed to be spheres, there are

TABLE 3

Variation in shape constant ratio for different geometric shapes

a is length; *b* is dimension at right angles to *a*; *c* is thickness

SHAPE	SURFACE	f_s	VOLUME	f_v	K
Disc: $a = b$	$\pi b(b/2 + c)$		$\pi b^2 c/4$		
$c = 0.1b$		$3\pi/5$		$\pi/40$	24
$c = 0.2b$		$7\pi/10$		$\pi/20$	14
$c = 0.5b$		π		$\pi/8$	8
$c = b$		$3\pi/2$		$\pi/4$	6
Plate: $a = b$	$2b(b + 2c)$		$b^2 c$		
$c = 0.1b$		2.4		0.1	24
$c = 0.2b$		2.8		0.2	14
$c = 0.5b$		4		0.5	8
$c = b$		6		1	6
Bar: $b = c$	$2b(b + 2a)$		ab^2		
$a = 10b$		42		10	4.2
$a = 5b$		22		5	4.4
$a = 2b$		10		2	5
$a = b$		6		1	6
Cube: $a = b = c$	$6b^2$	6	b^3	1	6
Sphere: $a = b = c$	πb^2	π	$\pi b^3/6$	$\pi/6$	6
Tetrahedron: $a = 1.16b = 1.23c$	$2.3b^2$	2.3	$0.18b^3$	0.18	13
Cone: $a = b = c$	$0.81\pi b^2$	0.81π	$\pi b^3/12$	$\pi/12$	9 7
Double cone: $a = 2b = 2c$	$1.12\pi b^2$	1.12π	$\pi b^3/6$	$\pi/6$	6.7

relatively few papers in which the authors have attempted to evaluate shape in absolute terms. Green (23, 24) was one of the first to discuss the necessity for considering the shape in relation to volume and surface. Heywood (26, 27, 28) has measured the surface and volume of relatively large particles. From these results he proposed shape factors based on the projected area of the particle and its thickness but, as might be expected, these relations become exceedingly complex in defining surface and volume. Furthermore, there is no

reason to assume that the relations for macroscopic particles apply to microscopic ones. It is quite possible that, as subdivision takes place, the particles tend to lose the shape of the mass from which they were derived and may or may not become spheroidal.

Wadell (48) has proposed a degree of sphericity which is the ratio of the surface of a sphere of diameter, d_n, to the actual surface of the particle and is equal to $\sqrt{36/s}$, where s is the area of a solid having unit volume but the same shape as the particle. When the particles are in the microscopic range, it appears that such a treatment is too difficult to use.

Dalla Valle (13) and Dalla Valle and Goldman (14) have studied the individual shape factors for silica, using the treatment of Hatch and Choate (25) for estimation of the mean size. The surface shape factor (the number required to convert the square of the mean diameter to actual surface) was determined from the pressure–drop relation of Burke and Plummer (10) for fluids passing through a column packed with the material. The volume shape factor (the number required to convert the cube of the mean diameter to actual volume) was determined by direct count of a weighed amount of particles. Their results

TABLE 4

Evaluation of shape constant ratios for various types of materials

TYPE	FORM	EXAMPLES	K
Regular....	Cubical	Galena	6–8
Angular.	Tetrahedron	Silica, coal, cement	6–12
Acicular	Bar, cone	Slate, talc	4–10
Platelike	Plate, disc	Mica, talc	6–14

showed the surface shape factor to be less than π and the volume shape factor to be less than $\pi/6$. These values set as a maximum are those of a sphere and represent a convenient datum for studying shape factors but do not represent the maximum values, as shown in table 3.

The principal purpose in evaluating particle shape is for the determination of specific surface. As will be shown later, specific surface is directly proportional to the ratio of the surface shape factor, f_s, to the volume shape factor, f_v. If f_s and f_v are defined as the factors which relate the surface and volume of a particle to the square and cube, respectively, of its diameter, the problem is simplified and allows greater practical application of these functions than is possible with those proposed heretofore. If the shape constant ratio, K, is defined as the ratio of f_s/f_v, it can be shown readily that K does not vary greatly for various smooth geometric shapes. This is illustrated by the data in table 3, which show that the shape constant ratio lies between 4 and 14 for geometric shapes that are probably representative of the shapes approached by particulate materials. From a knowledge of the characteristics and microscopic dimensions of such particles it is then possible to assign values for their shape constant ratios to various types of materials. In this manner a more logical estimation

of specific surface may be made than to assume a value of 6 (for a sphere) in all cases. Such an estimation of shape constant ratios has been made in table 4.

The advantage of this method of treating the shape function is that the evaluation of one shape constant ratio eliminates the separate determination of the individual surface and volume constants. Furthermore, the shape constant ratios are not subject to as great variations as are f_s and j_v (see table 3). Values for K based on microscopic inspection of the dimensions of representative particles of the closely fractionated materials used in this study were estimatde as given below, assuming a smooth surface:

MATERIAL	K
Silica, D-2	8
Slate, 470	7
Mica, 432	14
Coal, C	8
Galena, G	6

C. STRUCTURE

The surface configuration of a particle also has an important effect on its industrial use, since the structure may vary from the smooth surface of galena, figure 1F, to the porous structure of diatomaceous earth, figure 1H. The structure may exert its influence in the scattering of radiation (visible, infrared, etc.) to which it is exposed or in the actual surface exposed to chemical reactions. Structure is a difficult property to evaluate, and until its relations to other properties are first established it cannot be evaluated. The shape factor ratio, K, by definition includes both shape and structure considerations; this indicates that a combination of both these properties might be evaluated indirectly by such means as adsorption or light scattering.

D. SIZE DISTRIBUTION

The preceding discussion relates mainly to the study of the properties of individual particles; in industrial practice, however, the principal emphasis is on the properties of mixtures of particles either of a large size range or a rather closely sized fraction. Thus, the size distribution becomes a primary property in describing the characteristics of a powder, since it affects the secondary properties. The principal means of evaluating size distribution is to determine a weight distribution, i.e., to obtain the per cent by weight between certain size limits. From such a distribution the suitability of a material for a particular purpose may be ascertained by inspection of the size-distribution curve cr by calculation of some property in quantitative terms, such as specific surface or a uniformity coefficient.

A plot of cumulative per cent undersize *versus* log diameter is a relatively simple means of comparing size-distribution data and allows rapid estimation of the adaptability of a material for a particular use. Such plots have been

used in comparing the weight distributions for the studies of microscopic diameters shown in figure 2. In addition, there are shown the size distributions obtained from sedimentation data for the same five materials. The turbidity data were converted to size distribution according to the method of Wagner (1). For these rather closely sized materials a constant transmittancy constant for all sizes, as used by Wagner, was assumed valid. With the closely fractionated materials used in this study the theoretical treatment of Wagner appears valid, on the basis of the results for d_s and d_t shown in table 1.

Other graphical methods for showing size distribution have been proposed, and a review of them has been given by Austin (6). This author presented the mathematical relations for evaluating size distribution and recommended the use of log probability curves. For many materials the data approximate straight lines, but this treatment tends to desensitize the data to a considerable extent. In addition, these plots will not apply rigorously to the size distributions of certain materials, depending upon the operations used in their production. In such cases a cumulative per cent undersize *versus* log diameter plot[2] will show the correct size distribution and a frequency-log diameter curve, such as per cent per micron *versus* log diameter, will be still more sensitive to slight variations in distribution. Heywood (27) has proposed a modified frequency plot in which the coördinates are corrected for mean size, thus allowing materials of considerable difference in size to be plotted on the same chart for comparisons of size distribution. Work (56) has proposed a frequency–diameter plot consisting of a primary and secondary relation which can be reduced to a single equation. Roller (39) has proposed a similar type of plot. Both these equations are more complex than the log probability types, but significant peaks in the distribution are not smoothed by desensitization. Vieweg (47) has suggested a method of evaluation based on the reciprocal of the fourth power of the diameter.

The degree of precision of the size measurement is the limiting factor in the use of sensitive frequency distribution plots and consideration must be given to the use of the plot for interpretation of the results before any one type of curve is selected. Thus, for control work it is necessary that a rapid evaluation of the size distribution be obtained, and complex plots are not suitable.

Other methods of quantitatively evaluating size distribution are those in which some mean diameter is calculated, such as a surface mean diameter, D_s:

$$D_s = 100/(\Sigma G_f/d_m), \text{ microns} \tag{3}$$

where G_f is the weight per cent in the individual fractions, and d_m is the arithmetic mean of the limits of the fractions, in microns.

In a similar manner a weight mean diameter, D_W, may be obtained from:

$$D_W = (\Sigma G_f d_m)/100, \text{ microns} \tag{4}$$

---

[2] In drawing the curve for a cumulative per cent curve, the nature of the curve demands that all points be connected rather than that a smooth curve be drawn between all points, if the precision of the method warrants it.

It can be shown by experiment that D_w from equation 4 is the size at which there is 63 per cent by weight finer for a wide variety of materials. The size at 63 per cent finer is a parameter of the Rosin–Rammler equation, as given by Austin (6). Since it is a distribution constant, it probably can be derived from equation 4 and the Rosin–Rammler law. This has been attempted without

TABLE 5

Comparison of D_w and d_{63}

MATERIAL	WEIGHT MEAN DIAMETER D_w	SIZE AT 63 PER CENT FINER d_{63}
	microns	*microns*
Jaw-crusher feed		
Traprock	7.750	7,300
Limestone	21,200	20,900
Jaw-crusher product (classified)		
Limestone	11,800	11,200
Mica schist	9,400	8,400
Roll-mill product (classified)		
Limestone	3,130	3,150
Ball-mill product		
Traprock (1 hr.)	281	65
Mica schist (1 hr.)	159	150
Limestone, 957	55	50
Plus 40-micron material	100	110
Minus 40-micron material	16	19
Red slate, 642	11	13
5–10 micron fraction	9	10
20–40 micron fraction	38	31
Green slate, 470	17	12
Traprock, 113	25	30
Pumice, 571	11	10
Green mica, 432	18	17
Talc, 573	18	19
Diatoms, 939	13	11
Silica, 196	21	22

success, although Hottel and Stewart (29) have derived an analogous relation for studies on coal. Experimental data are given in table 5, comparing D_w and the size at 63 per cent finer. With the exception of one or two materials, the results are in good agreement, indicating the general applicability of selecting the mean size at 63 per cent passing without recourse to computation by equation 4. In the case of the ball-mill traprock ground for 1 hr. the results do not agree, but neither is the Rosin–Rammler plot a straight line. This is to be

expected if the effects of the size distribution of the feed are not eliminated by sufficient grinding. The feed effects can be illustrated by a frequency plot of such materials which will show a double peak. The peak in the coarse size range has a great effect on the weight mean diameter, and, accordingly, D_w is not equal to the size at which there is 63 per cent undersize. The type of material being ground also has an effect on the time required to reduce the peak in the coarse size range to a normal distribution, as is shown by the results for the mica schist ball-mill product ground for the same time. The feed size of the traprock was minus a No. 6 sieve and plus a No. 35 sieve, while that for the mica schist was minus a No. 8 sieve and plus a No. 35 sieve.

It can be shown readily that an infinite number of size distributions may give the same numerical values for either of the two mean diameters given by equations 3 and 4. However, in evaluating the properties of a series of materials produced in the same manner, these mean diameters are satisfactory to use if the same fraction limits are applied in each case.

A finely divided material may be further described by computing the uniformity, i.e., the range of the property compared to the mean. Briefly, these relations may be computed from the equation

$$A = \sqrt{\frac{\overline{(D - \overline{d_m})^2 F_f}}{\Sigma F_f}} \tag{5}$$

where A = the standard deviation,
        D = the mean diameter of the whole powder based on F,
        d_m = the mean diameter of each fraction, and
        F_f = the value of the property for each fraction and may be number, surface, or weight.

The deviation can then be corrected for actual size (24) by computing the uniformity coefficient, U, where the terms are the same as in equation 5:

$$U = D/(A\sqrt{2}) = 0.71D/A \tag{6}$$

Certain other arbitrary methods are used to evaluate the spread of sizes, such as the uniformity coefficient used for filtration sands:

$$U = d_{60}/d_{10} \tag{7}$$

where d_{60} and d_{10} are the sizes which show 60 and 10 per cent finer, respectively, as interpolated from a cumulative per cent versus diameter curve.

The final choice in selecting methods for evaluating size distribution is dependent upon the use to be made of such information. The most expedient ones to employ are those that yield the necessary information to differentiate materials the properties of which are similar in other respects but which behave differently when used in a particular product.

II. Secondary Properties

A. SURFACE

The surface of a particle or of a group of particles is dependent upon the primary properties previously discussed. In general, it is evaluated for groups of particles having a more or less wide range of sizes.

The surface of the particles can best be defined as the specific surface, $\underline{S}$, which is the surface possessed by a unit weight and is generally expressed as square centimeters per gram. It may be calculated by means of the following equation (cf. equation 3):

$$\underline{S} = \Sigma \underline{S_f} = \Sigma \frac{KG_f \times 10^2}{D_s \times d_m} = \frac{K \times 10^2}{D_s} \Sigma G_f/d_m = \frac{K \times 10^4}{D_s \times D_s} \quad (8)$$

where $\underline{S_f}$ = the surface in the individual fractions per gram of whole powder,

K = the shape ratio constant (f_s/f_v),

G_f = the weight per cent in the individual fractions,

D_s = the density of the material, in grams per cubic centimeter,

D_S = the surface mean diameter (equation 3), in microns, and

d_m = the arithmetic mean diameter of the limits of the fraction, in microns.

The above equation assumes that the mean particle size of the fraction is at the midpoint of the fraction; this is a valid assumption provided the spread of sizes is not very great in the small size ranges. It is an expedient treatment to use for surface computations where the weight distribution is known. However, it requires knowledge of the ratio of the surface-to-volume shape constant, K. In most published work, this constant has been assumed as $\pi/(\pi/6)$, or 6, which is the value for a sphere, but in the approach to absolute evaluation of specific surface it is necessary to assign more accurate values to this constant for different types of materials.

One of the principal uses of the per cent per micron versus log diameter plot is for the estimation of surface, since the area under such a curve is directly proportional to specific surface, as was indicated by Roller (38).

If G is cumulative weight per cent and ΔG is the weight per cent between two diameters, ΔD, then the per cent per micron is $\Delta G/\Delta D$ and the area, A, under the curve is

$$A = \int dA = \int (dG/dD)\cdot d(\log D) = (1/2.3) \int (dG/dD)\cdot(dD/D)$$
$$= (1/2.3) \int dG/D \quad (9)$$

The volume of a particle is $f_v D^3$. Its weight, W_f, is $f_v D^3 D_s$, if D_s is the density. Its surface is $f_s D^2$. The surface, therefore, in square centimeters for D in microns is given by

$$S_f = \frac{f_s W_f \times 10^4}{f_v D_s \times D} = \frac{KW_f \times 10^4}{D_s \times D} \quad (10)$$

where K is the shape constant ratio, f_s/f_v.

The specific surface, $\underline{S}$, in square centimeters per gram is equal to the sum of the individual surface from each fraction given by equation 10 divided by the total weight of the material, or

$$\underline{S} = \Sigma S_f/\Sigma W_f = \frac{K \times 10^4}{D_s \times \Sigma W_f} \times \Sigma W_f/D \quad (11)$$

But $(W_f/\Sigma W_f) \times 100$ equals ΔG; therefore

$$\underline{S} = \frac{K \times 10^2}{D_e} \times \Sigma \Delta G/D = \frac{K \times 10^2}{D_e} \int dG/D \qquad (12)$$

or

$$\underline{S} = \frac{2.3 \times K \times 10^2 \times A}{D_e} \qquad (13)$$

The numerical value of A may be obtained by means of a planimeter or by the more approximate graphical integration

$$A = \Delta(\Delta G/\Delta D) \times (\log D)_a \qquad (14)$$

where $\Delta G/\Delta D$ is the per cent per micron at $(\log D)_a$, the latter being the arithmetic average of the logs of the limiting sizes of the fractions.

The specific surface as computed by equation 13 is somewhat more accurate than the results from equation 8, since inflections in the size-distribution curve are magnified. For the same reason the use of equation 13 necessitates methods for determining size distribution that yield close fractionation with a higher degree of precision. In practical applications, equation 8 is recommended because, in general, the methods for measuring particle-size distribution that are available lack the precision required for equation 13 and, in addition, the use of equation 8 is less laborious. Another graphical method for obtaining the specific surface is by means of the Gates diagram (21), which is a plot of cumulative per cent finer *versus* the reciprocal of the diameter. It can be shown readily that the area under such a curve is proportional to surface, since the area equals $\int_0^{100} dG/D$.

In addition to the above methods of determining surface from weight-size distributions, means have been proposed for estimating the gross surface of the powder other than from the surface of the individual fractions. Emmett and coworkers (17) have evaluated surface by adsorption isotherm data which, when compared with results from hydrometer analysis on soils, gave "a little higher results." Askey and Feachem (5) have used a similar method. Other methods for estimating specific surface from permeability data have been proposed and will be discussed under packing properties. For other indirect methods used to estimate surface, reference should be made to the bibliographies of Roller (40), Work (55), and Heywood (27). Such methods do not yield information regarding the size distribution, as actually an infinite number of distributions may yield the same specific surface.

A computation of specific surface by means of equation 8 was made for the five closely fractionated materials studied previously, wherein G_f was made equal to 100 and d_m was the measured mean diameter. The results are shown in table 1, where the necessity for standardized procedures for evaluating particle size and shape is evident. Thus, the relative surface shown by silica and mica will be considerably different, depending upon whether settling diameter or microscopic diameter is used as the criterion. Furthermore, their relative sur-

face based on any given diameter will depend upon the value of K used. If different types of particles can be classified as to their general shapes, it will then be possible to evaluate K and in turn the specific surface in terms which will be an approach to absolute values.

B. PACKING PROPERTIES

A secondary property that is used to a considerable extent in industry for evaluating finely divided materials is their packing or bulking properties. Such evaluation may take one of a number of forms. The bulk density, B_c, may be defined as the ratio of the volume (particles plus voids) occupied by a unit weight of the material. Such determinations when used for comparison should be made under the same conditions to get the same degree of compaction. A simple method of determining the bulk density consists in filling a 100-cc. graduate to the top with the dried material and then compacting it by allowing the graduate and contents to bounce on a rubber-covered brick. These operations are continued until the volume no longer decreases. In general, this end point is denoted by a definite change in the sound created by the compacting operation. Such a compaction may be considered to be "to completion," and from the observed volume and the weight of the material the bulk density and per cent voids may be calculated. For obtaining the compacted weight of materials in the loosely compacted state, the Scott volumeter is suggested. In this apparatus the powder is allowed to flow at a uniform velocity into a small box of known volume. From the weight of the powder the bulk density, B_l, can be computed for the loose condition of packing.

In order to compare materials of different true densities, D_a, it is expedient to calculate the per cent voids in the compacted mass. The per cent voids, V, may be calculated from the bulk density by means of the following equation:

$$V = 100(1 - B/D_a) \qquad (15)$$

Traxler and coworkers (44) give a discussion of the packing of mineral powders, as do also Work (55), Roller (37), and Burmister (11). These methods are suggested for use only as approximations in evaluating relative sizes, since size distribution and particle shape have a considerable effect on the results. The effect of size distribution is used by Anderegg (1) in selecting gradings for desired densities. The mathematics of the packing of spheres has been discussed by White and Walton (54) and by Manegold and coworkers (31, 32), but the application to irregular shapes is quite complex. These packing properties have been used to a considerable extent in evaluating the properties of fillers used for asphalt, in studies of aggregates used for concrete, and in powder metallurgy.

A more elaborate test of compacted mineral powders consists in the evaluation of the permeability of the compacted mass from pressure drop relations. Traxler and Baum (45) determined the average void diameter for different ground minerals and indicated that it was related to the average particle size of the material. A compilation of such data and other properties of various

TABLE 6
Typical particle-size data on various materials

MATERIAL	NO.	D_s	D_S*	D_W	B_a	V	d_v
		grams per cc.	microns	microns	grams per cc.	per cent	microns
Limestone.....................	107	2.73	6.4	29	1.78	34.6	1.14
Traprock......................	113	2.91	6.3	25	1.58	45.6	1.63
Coal..........................	C	1.75	9.8		1.18	33.0	
Galena........................	G	7.66	15		4.94	35.6	
Glass spheres†	S1	2.50	127	129	1.48	40.8	40.6
Glass spheres‡	S2	2.50	94	95	1.49	40.3	29.2
Mixed glass spheres		2.50	133		1.59	36.2	34.7
Asbestos	38	2.61			0.92	65.0	
Zinc powder§..................	2196	7.07			4.16	41.1	2.46
Aluminum powder§...........		2.70			0.75	72.5	
Titanium dioxide§.....	TO	4.10			0.72	82.5	
Silica.........................	196	2.62	5.5	21	1.64	37.5	1.07
0–2 microns..		2.62	1.2		0.92	65.2	1.01
2–5 microns.....		2.62	3.9	4.2	1.24	52.7	1.20
5–10 microns		2.62	7.7	8.4	1.37	47.5	2.07
10–20 microns		2.62	15	16	1.47	44.7	2.85
20–40 microns		2.62	31	33	1.45	43.7	6.02
40–80 microns..............		2.62	59	61	1.44	44.1	9.08
Black slate....................	197	2.91	5.1	9.9	1.24	57.4	1.66
0–2 microns.................		2.91	1.0		0.84	71.8	1.01
2–5 microns..........		2.91	4.8	5.1	0.87	70.3	1.16
5–10 microns.		2.91	7.5	7.6	0.97	66.6	1.72
10–20 microns..............		2.91	12	12	1.06	63.6	2.52
20–40 microns..............		2.91	18	19	1.14	60.9	3.85
40–80 microns..............		2.91	44	45	1.32	54.8	7.00
Red slate.....................	642	2.80	2.2	11	1.30	53.4	0.87
5–10 microns.................		2.80	8.1	9.3	1.49	46.7	2.26
20–40 microns..............		2.80	34	38	1.54	45.2	6.64
Green slate...................	470	2.82	3.9	17	1.21	57.0	1.27
Green slate	471	2.82	3.2		1.02	63.8	1.30
Cement........................	2135L	3.08	6.7¶	13.1	1.44	53.3	1.83
Cement........................	2194NA	3.14	7.4¶	16.3	1.58	49.7	1.58
Green mica....................	432	2.92	9.2¶	18	0.89	69.5	1.30
Diatoms....:..................	939	2.19	4.8¶	13	0.48	78.3	2.63
Talc..........................	573	2.82	10.8¶	18	1.12	60.2	1.31
Pumice........................	571	2.38	5.7¶	11	1.00	58.0	1.66
Tripoli........................	223	2.60	7.8¶		1.20	53.7	2.04

* Data for fractions of 196, 197, 642 and glass spheres are based on microscopic counts; others on sedimentation analysis.

† Minus No. 100 sieve plus No. 140 sieve.

‡ Minus No. 140 sieve plus No. 200 sieve.

§ Commercial product.

¶ Air-elutriation data.

materials is given in table 6. The fractions of whole powders were obtained by means of a Federal pneumatic separator (18).

The calculation of specific surface (or average particle size) from permeability data has received considerable attention recently, because of the speed with which the results may be obtained. These methods are based on an empirical relation proposed by Carman (12) for relating surface and pressure drop through packed solids. The results for the specific surface of silica (5420 sq. cm. per gram) and of black slate (7040), calculated from permeability data of Traxler and Baum (40), are considerably higher than similar results (4150 and 4050, respectively) computed from sedimentation data assuming spherical shape with K equal to 6. Lea and Nurse (30) have proposed a similar method for evaluating specific surface based on Carman's work but using gases instead of liquids, as was done by the latter. These investigators indicated that liquids tend to give high results, although their values using air for cement and ground sand were about 20 per cent higher than the results computed from size-distribution data obtained by pipet analysis. By using Andreasen's relation (discussed under sedimentation diameter), the authors showed that the results by the two methods could be made to agree by multiplying the settling diameter by 0.806. The net result of this correction is to evaluate specific surface in terms of a diameter reduced to a hypothetical sieve dimension equivalent to the settling diameter. Such a basis for surface evaluation is not tenable, since, as was illustrated in table 1 and as has been shown by others, all data point to the fact that the actual size is greater than the sieve dimension. In most cases permeability surface tends to give higher results (42) than specific surface results calculated from size-distribution data obtained by other methods. The variations are caused by considerations of the shape constant ratio, K, and the values used for the Carman empirical constant in converting permeability data to surface.

In connection with permeability measurements, it should be pointed out that a gross size function only is measured, and no data are obtained on size distribution. These empirical methods of Carman, Lea and Nurse, and Gooden and Smith (22), all of which are similar, may apply for selected powders, but they cannot be used with confidence until the relations between packing (a secondary property) and the primary properties are rigorously established. Permeability analysis would appear to offer interesting possibilities in evaluating particle shape and the rapid estimation of specific surface for control purposes. Such methods are particularly adaptable to studies of mixtures of materials of different densities, which otherwise require microscopic counts or special apparatus and techniques.

III. CONCLUSIONS

From the results of this investigation the following conclusions were drawn:

1. For many materials, the d_b diameter (shorter of the two visible microscopic dimensions) yields essentially the same results as the d_k diameter (square root of the projected area). An exception was micaceous material, for which the former gives lower results; for the particular mica used in this study the ratio of d_b/d_k was about 0.9.

2. On the basis of the results for a No. 325 sieve (nominal aperture 44 microns), the mean d_b dimension of particles just passing may vary from 1.2 to 1.5 times the aperture.

3. The mean sedimentation diameter (diameter of the equivalent sphere) varies from 0.5 to 0.9 of the d_b dimension, depending upon the material. This variation accounts for the discrepancies between the results for particle-size distribution obtained by microscopic counts and those from sedimentation methods.

4. While the mean sedimentation diameter of particles just passing a No. 325 sieve may vary from 0.8 to 1.2 times the sieve aperture, the separation point for most materials may be taken as 53 microns or 1.2 times the aperture, since the point of separation in reality measures the upper limit of the material just passing. A single sieve correction factor (1.2 times the aperture) may be used expediently for all materials for which combined sieve and sedimentation analyses are employed, in order to put the entire analysis on a sedimentation diameter basis.

5. In practice it is not necessary to determine individual surface and volume shape factors if the shape constant ratio is known, since the latter is sufficient for the computation of specific surface from weight distribution.

6. The average weight diameter, D_w, is equal to the size at which there is 63 per cent undersize for many pulverized materials, indicating that this size, which is a parameter of the Rosin–Rammler law, is a significant property of such materials.

7. Empirical methods for evaluating specific surface from permeability data cannot be used with confidence until the basic relations between packing (a secondary property) and the primary properties are established.

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THE DIELS–ALDER DIENE SYNTHESIS

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CONTENTS

I. INTRODUCTION

A. Definition

The diene synthesis (often termed the Diels–Alder reaction or the Diels–Alder diene synthesis) is more than the name implies. Enynes and diacetylenes may also undergo typical diene synthesis reactions. Basically, the great majority of these syntheses may be classified under one of the following types:
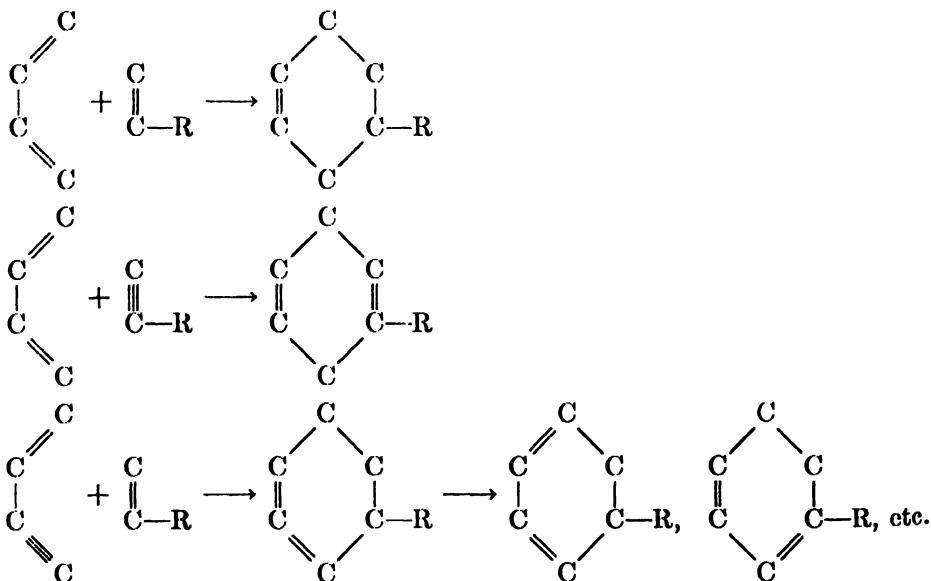
R in the above examples is usually of the types which terminate in a carbonyl group attached directly to one of the olefinic or acetylenic carbon atoms. Repre-

sentative dienophiles of this type are acids, their anhydrides, esters, and halides, and also aldehydes, ketones, or quinones. The carbonyl group is not a necessary structural feature, however. It will be shown later that R may be acetoxyl (as in vinyl acetate), nitro, sulfonyl, cyano, amino, vinyl, or even hydrogen. Diene syntheses proceed with greatest facility, however, when R contains the carbonyl group in the manner indicated above.

B. Nomenclature

The compound which acts in the capacity of $C=C-R$ or $C\equiv C-R$ is designated as the *philodiene* or *dienophile*; the latter term seems less confusing. The etymology of these terms from the Greek is apparent. The other compound involved in the reaction, whether it be diene, polyene, enyne, or diyne, will be referred to as the *diene* in this review purely for the sake of convenience. The reaction product is the *adduct* or *adject*. The *diene* and *dienophile* are often designated collectively by the term *generators*.

C. Dienes

The forms which the diene may assume are amazingly variable. For instance, the diene may be simple, as piperylene or isoprene; or it may be more complex, as furan, pyrrole, thebaine, tetraphenylcyclopentadienone, pyridine, anthracene, ergosterol, cycloheptadiene, α-naphthylacetylene, 3,4-dihydro-1-vinylnaphthalene, 1,3-menthadiene, or 1,2,5,6-dibenzanthracene. Neither thionessal (tetraphenylthiophene) nor thiophene itself has been observed to add dienophiles, and the same is probably true of the thiotolenes, thioxenes, and selenophene. The whole subject of non-addition of dienophiles by thiophene and its derivatives has, however, been reopened by Clapp's discovery (400) that one compound of this series will add dienophiles at temperatures in the neighborhood of those employed for sulfur dehydrogenation of hydroaromatic compounds. In the investigations of the other thiophene compounds it is doubtful that the temperatures used by Clapp were employed. Clapp's reaction occurs with the evolution of hydrogen sulfide as in a sulfur dehydrogenation, and it may be that other thiophenes will respond under similar conditions.

Benzene and its simpler derivatives have been observed not to add dienophiles. Compounds do exist, however, in which one of the diene double bonds is a Kekulé double bond. Anethole and α-phenylstyrene are compounds of this type; they add maleic anhydride with reduction of one of the benzene rings to a cyclohexadiene ring. α-Vinylnaphthalene acts in a similar manner. One example (9,10-anthraquinone) appears to be known in which a lone benzene ring is able to add dienophiles, but this is disputed by a negation published prior to the above report. Heterocyclic dienes containing nitrogen as a part of the ring (pyrrole or pyridine) invariably react abnormally. Elsewhere the diene synthesis usually gives products the formulas of which are in accordance with the general statement of the synthesis as given by the reaction types on page 320. It is occasionally found that certain compounds containing isolated double bonds, one double bond, or even no double bonds at all will add dienophiles.

This phenomenon usually can be explained by assumption of a preliminary isomerization or conversion of the compound in question to another substance containing isolated double bonds, and eventually to one containing conjugated double bonds which is able to add the dienophile. Such examples are found almost exclusively among the terpinoids.

Occasionally the adduct will decompose in a predictable manner when heated, or upon formation if the temperature of the reaction mixture of diene and dienophile is sufficiently high. Adducts of acetylenic dienophiles with cyclohexadienes, cyclopentadienones, and derivatives of the lactone of 1-hydroxy-1-carboxy-1,3-butadiene (cumalin) evolve ethylenes, carbon monoxide, and carbon dioxide, respectively, when pyrolyzed.

Only a limited number of enynes has been studied. Butz has done most of the existing work in this field which, though not well developed, offers considerable promise.

At least one phase of the well-known trimerization of acetylene to benzene might be regarded as a diene synthesis. This phase would be the addition of a mole of acetylene to the dimer of acetylene (vinylacetylene), yielding benzene. It should be said that there is apparently no conclusive proof that the trimerization proceeds through such a mechanism; but since no proof of any other definite mechanism appears to have been established, the author feels that the mechanism of the diene synthesis for the formation of benzene is as admissible for consideration as any other mechanism.

D. Allenes

Dienes containing the grouping $C{=}C{=}C$ do not react directly with dienophiles. Reaction is possible through the mechanism of an initial isomerization to a conjugated system, such as could occur at elevated temperatures. A few allenes have been studied; thus, 1-cyclohexyl-2,3-pentadiene (2) was found not to react with maleic anhydride (see also 403, 404).

E. Tests for dienes

Since a transient yellow color is observed in the reaction of maleic anhydride with dienes, it had been proposed that the appearance of such a color on treatment of an unknown substance with maleic anhydride was a positive test for a conjugated dienoid system. Sandermann (323, 324) found that the test was unreliable, since positive results were secured with resorcinol, hydroquinone, pyrocatechol, benzidine, diethylaniline, diphenylamine, brucine, anethole, and carbazole, as well as with ergosterol, α-phellandrene, abietic acid, isoeugenol, anthracene, and pyrene. Apparently a negative test is of more value than a positive test.

The Fieser test (203) for conjugated dienes consists in treating the unknown with a solution of diazotized p-nitroaniline. If an orange color develops within a reasonable time, the test is positive. Arbuzov and Rafikov (60) believe the test to be unreliable, for in the reaction of dienes with the Fieser reagent some dinitrodiazobenzene is always formed. The structure of the coupling product

with butadiene (60) is probably *p*-nitrobenzeneazo-1-butadiene, for reduction gives *p*-phenylenediamine and pyrroline. Goodway and West (229) obtained positive tests using caryophyllene, *α*- and *β*-phellandrenes, *α*-pinene, 3-carene, and dipentene. Save for the phellandrenes, not one of these compounds contains a conjugated system.

F. trans-Butadienoid systems

The Bredt addition rule (322, 324) postulates that in cyclic dienes, the two double bonds must be in the same ring in order that addition of dienophiles may occur according to the diene synthesis. In contradiction to this rule, it is found that bis-1-dialin (3,4,3′,4′-bis(dihydro-*α*-naphthyl)) adds dienophiles without double-bond wandering prior to addition; and many other similar examples may be found, such as the addition of dienophiles by 2,3,4,5,2′,3′,4′,5′-octahydrobiphenyl. The rule should be modified by stating that the two double bonds of the conjugated system must be in the *cis*-configuration with each other or else must rearrange to such a configuration before addition can occur. In the majority of cases free rotation of the single bond between the 2- and 3-carbon atoms of the butadienoid portion of the molecule makes assumption of either a *cis*- or a *trans*-configuration a simple matter. In certain cases, however, only a *trans*-butadienoid system may exist without placing a large amount of strain on the molecule. The *trans*-butadienoid systems of *β*-phellandrene and 3,5-cholestadiene (cholesterilene) cannot well change into *cis*-butadienoid systems without double-bond migration. Addition to these molecules proceeds with great difficulty and probably with rearrangement and polymerization. Thus, *β*-phellandrene and maleic anhydride give tars and a small yield of the adduct of *α*-phellandrene and maleic anhydride. The adduct is obtainable only on vacuum distillation of the tar (228). Cholesterilene (332) adds maleic anhydride (348) only under drastic conditions to give a product the alkali salts of which are insoluble in water (distinction from other sterol-maleic anhydride adducts), and which are probably polymeric. Certain other sterol dienes of *trans*-butadienoidal configuration have been shown not to react with maleic anhydride (405).

II. DISCOVERY OF THE DIENE SYNTHESIS

Isolated examples of the diene synthesis appear in the literature of the past half-century, but the extensive development of the subject did not begin until 1928, when Diels and Alder recognized that a reaction observed by Euler and Josephson (195) between *p*-benzoquinone and isoprene was strikingly similar to a reaction observed by Diels, Blom, and Koll (157)—of azodicarboxylic ester with cyclopentadiene and also with isoprene derivatives. That the reaction was possibly of general application can be sensed from the paper of Diels, Blom, and Koll, and apparently the years 1925–1928 were devoted to experimentation designed to show that such actually was the case.

An early series of papers by Zincke and coworkers (376–378) dealt with the reactions of 1,2,4,5,5-pentachlorocyclopenten-3-one. Loss of a molecule of

hydrogen chloride from this compound gave tetrachlorocyclopentadienone. Since this compound contains the structures of reactive diene and reactive dienophile, it was not isolated as such, but rather as the dimer which was formed according to the Diels–Alder diene synthesis. The dimer was an intermediate product in a series of reactions ending in octachlorohydrindone, which was easily reduced to hexachloroindone.

Staudinger (337) has made a very famous series of researches on polymerization and on compounds of high molecular weight. It was his opinion that the dimerization of cyclopentadiene occurred to give compounds containing cyclobutane rings. The dimer of cyclopentadiene was considered to be the product of the 1,2-addition of two molecules of monomer to each other. The structure of such a product would be that of a cyclobutane with two cyclopentene rings fused to it. In a brilliant series of papers on the structure of cyclopentadiene polymers, Alder and Stein showed that these were formed by the 1,4-addition of a molecule of cyclopentadiene to a double bond of cyclopentadiene monomer or polymer. The structure of cyclopentadiene dimer (dicyclopentadiene) is that of a partially hydrogenated indene possessing a methylene bridge across the 4- and 7-positions. 1,4-Addition of cyclopentadiene to this compound occurs at the double bond of the six-membered ring, giving cyclopentadiene trimer. In the production of higher polymers, 1,4-addition of cyclopentadiene to its polymer always occurs at the double bond of the terminal six-membered ring and never at the double bond of the five-membered ring.

Albrecht (379) described, in 1906, certain experiments in which cyclopentadiene was caused to react with quinones and ketones. The reaction product of p-benzoquinone with an equimolecular quantity of cyclopentadiene was thought to be I. While the structure of the C_5H_5 group was not stated explicitly,

I   II   III
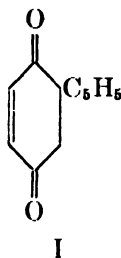
it probably was intended to be as shown in formula II, for cyclopentadiene forms a potassium derivative (III).

Albrecht was not altogether certain of the validity of structure I for his product. He also found that a second mole of cyclopentadiene would react with p-benzoquinone; the structure assigned to this product was that of 2,5-bis-cyclopentadienyl-tetrahydro-p-benzoquinone, although he recognized the possibility of 2,6 and 2,3 isomerism. Other quinones, such as chloranil and 1,4-naphthoquinone, were shown to react. A period of 2 hr. was required for the reaction of p-benzoquinone with a benzene solution of cyclopentadiene at

0°C., while chloranil required two weeks; both chloranil and 1,4-naphthoquinone would react with only 1 mole of the diene. 9,10-Anthraquinone, 9,10-phenanthrenequinone, β-naphthoquinone, benzil, benzalacetone, dibenzalacetone, phorone, and dibenzoylstyrene would not react under the mild conditions used. Since that time it has been found that β-naphthoquinone and the unsaturated ketones will react at higher temperatures.

Staudinger's work suggested that the condensation product of cyclopentadiene with p-benzoquinone was analogous to the dimer obtained from cyclopentadiene, for the structure he assigned to the condensation product was that of a compound formed by addition of cyclopentadiene and p-benzoquinone by the 1,2-addition mechanism.

In 1920, Euler and Josephson (195) published the paper already referred to, which concerned the reaction of isoprene with p-benzoquinone. The product obtained was assigned the structure of 2,6-dimethyl-1,4,5,8,1a,4a,5a,8a-octahydro-9,10-anthraquinone. This structure was nearly correct, for it was shown later (153) that the product was really a mixture of the 2,6- and 2,7-dimethyl-1,4,5,8,1a,4a,5a,8a-octahydro-9,10-anthraquinones.

The paper of Diels, Blom, and Koll (157) was next to appear. They paid particular attention to the structure of the reaction product that was obtained from cyclopentadiene and azodicarboxylic ester. In accordance with the assumptions of Albrecht, the structure of the product was first given as shown in formula IV. The assumptions of Staudinger led to formulation of the struc-
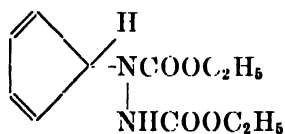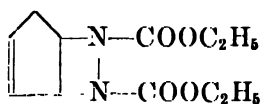
IV   V
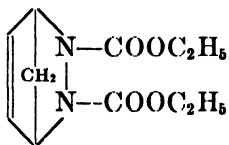
VI

ture as V, while the work of Euler and Josephson led to formulation of the structure as VI. Since the adduct took up only two atoms of hydrogen or bromine, structure IV was invalidated. Confirmation of formula VI was secured in several ways. First, the methylene bridge of the hydrogenated adduct (VII) was broken with hydrogen chloride to give a methylchloropiperidazine derivative (VIII). Secondly, the same hydrogenated adduct was saponified and decarboxylated to give an endomethylenepiperidazine (IX), vigorous reduction of which gave 1,3-diaminocyclopentane. No such compound could have been obtained from either compound IV or compound V.
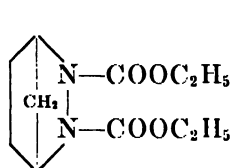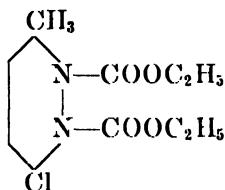
VII   VIII   IX

These facts threw grave doubts upon the Albrecht structure for the adducts of cyclopentadiene and *p*-benzoquinone, and furnished the initiative for the beginning of a program of research marked by the appearance of the first epochal paper by Diels and Alder (136). It should be noted that a considerable number of patents on the additions of dienes and dienophiles were taken out almost simultaneously by the I. G. Farbenindustrie A.-G.

In their first paper on diene syntheses, Diels and Alder presented evidence in support of their belief that Albrecht's addition compound between cyclopentadiene and α-naphthoquinone was 1,1a,4,4a-tetrahydro-1,4-endomethylene-9,10-anthraquinone, since the corresponding adduct between α-naphthoquinone and butadiene was easily oxidized to anthraquinone. Later (146) they were able to convert the cyclopentadiene adduct itself to anthraquinone, thus meeting the objections of Staudinger who insisted that the adduct was formed by 1,2-addition of cyclopentadiene to the quinone ring of α-naphthoquinone. The views of Diels and Alder concerning the structures of their products were the subjects of intense criticism at first, for it was thought that these might conceivably be "molecular compounds" somewhat akin to the compounds of the polynuclear hydrocarbons with picric acid, 1,3,5-trinitrobenzene, and styphnic acid. This view received apparent substantiation by the discovery that certain of the adducts would decompose into their generators on distillation. However, the formation of derivatives of anthracene could not be explained by the view which assumed that the adducts were so-called molecular compounds, and eventually the differing stabilities of individual adducts were made use of in the first preparation of the acid chloride of acetylenedicarboxylic acid (172) and in other ingenious, convenient, and useful syntheses.

The study of the diene synthesis has been pursued intensively since the publication of the initial papers of Diels and Alder. It is a matter of some difficulty to find a volume of a chemical journal of today which does not contain an article which bears on some phase of the diene synthesis. Today one sees polyesters the acid fractions of which are prepared by the diene reaction between abietic acid and maleic anhydride (304). By offering means for the quantitative determination of conjugated dienes in petroleum products, the diene reaction will facilitate the perfection of processes which produce motor fuels of initially high octane ratings and high lead susceptibilities combined with improved stabilities. The number of possible practical applications of the general principle of the diene synthesis is virtually unlimited.

III. DIENOPHILES

The types of compounds which may be used as dienophiles will be considered initially, for the majority of studies in the field of the diene synthesis were based primarily on the determination of the capacity of the compound under investigation to act as a diene in the diene synthesis. Since a considerable amount of work has been conducted with regard to quinones in the diene synthesis, these dienophiles will be discussed in the section to follow.

The types of dienophilic compounds which may be employed in the diene synthesis are nearly as diverse in character as the types of compounds which may serve as dienes. They may be added to the reaction mixture as such, or prepared *in situ* (47, 239).

A. Olefinic dienophiles

As stated previously, the dienophiles which add most readily are those containing the groupings $C=C-C=O$ or $C≡C-C=O$, and these have been the most extensively studied of dienophilic substances. With them, many diene syntheses occur readily at room temperature to give nearly quantitative yields of adducts. Examples of such dienophiles are crotonaldehyde, acrolein, 3,4-diketo-1-pentene, *sym*-dibenzoylethylene, 1-cyclopenten-3-one, acrylic acid, methyl acrylate, fumaroyl chloride, maleic anhydride, tetrolic acid, propiolic ester, acetylenedicarboxylic ester, *p*-benzoquinone, α-naphthoquinone, and *p*-toluquinone. With the exception of the nitrogen heterocycles, additions almost always occur in the manner indicated by the general rule for diene reactions as given on page 320. Thus, acrolein reacts with butadiene to give Δ^3-tetrahydrobenzaldehyde, and α-naphthoquinone and butadiene give 1,4,1a,4a-tetrahydro-9,10-anthraquinone (136). The nature of the solvent has no effect on the composition of the product, but ordinarily (196) reaction occurs about five times as rapidly in a polar solvent (ethanol) as it does in a non-polar solvent such as benzene.

Substituents located on the atoms of the carbon-to-carbon double bond (the "carbonylenic" (106) double bond) of the $C=C-C=O$ group definitely decrease dienophilic character. Two exceptions to this rule are the carbonyl group (as shown by the dienophilic property of ethylenetetracarboxylic ester) and groups which may split off easily during the course or after the completion of the diene synthesis (these are notably hydroxyl and the halogens). All other substituents, with the possible exception of the cyano group, tend to decrease the dienophilic property of the carbonylenic double bond.

The extent to which these substituents suppress dienophilic property depends to a great extent on the type of dienophile. These may be roughly divided into four classes:

Class A: Alkyl and aryl derivatives of acrolein, maleic anhydride, acrylic acid, and methyl or other alkyl or aryl vinyl ketones. These include such compounds as cinchonic anhydride, cinnamic acid, benzalacetophenone, crotonaldehyde, etc. The decrease of dienophilic activity is not of great magnitude, and is usually manifested only in cases of dienes of low reactivity or which have

groups on the 1- and 4-positions of the butadienoid system, when addition either is slow or fails to occur.

Class B: Fused-ring derivatives of acrolein, maleic anhydride, acrylic acid, and vinyl ketones. These include the adducts of equimolar quantities of diene and α,β-acetylenic acids and, generally speaking, all cyclene aldehydes, acids, and their derivatives, as well as cyclic ketones such as cyclopenten-3-one. Increase in unsaturation of the fused ring other than that of the carbonylenic group results in diminishing dienophilic properties. Thus, cyclohexene-1,2-dicarboxylic anhydride and 1,4-cyclohexadiene-1,2-dicarboxylic anhydride add butadiene with considerably greater difficulty than does maleic anhydride, while 1,3,5-cyclohexatriene-1,2-dicarboxylic anhydride (phthalic anhydride) has never been observed to add any dienes whatsoever.

Class C: Alkyl- or aryl-substituted quinones. Alkyl or aryl substituents of p-benzoquinone suppress the dienophilic activity of the carbonylenic group to which they are attached, but have little or no effect on the activity of the other carbonylenic group. Thus, p-toluquinone adds butadiene readily to give an adduct which does not possess an angular methyl group. This primary product of addition will add a second mole of butadiene to give an octahydroanthraquinone possessing an angular methyl group, but the addition takes place only with considerable difficulty.

Class D: Quinones with fused rings. These resemble Class B dienophiles. Thus, 1,4,5,8-tetrahydroanthraquinone will add dienes with considerable difficulty, and anthraquinone and phenanthrenequinone add no dienes whatsoever. However, fusion of two quinone rings to each other is actually the substitution of —CO— groups on a carbonylenic double bond, and therefore dienophilic activity is not suppressed. Naphthacenediquinone adds dienes almost as readily as does p-benzoquinone:
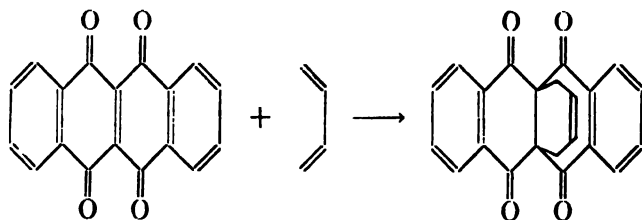
Naphthacenediquinone

To generalize broadly, it may be said that dienes and dienophiles will tend to react, as far as possible, to give adducts which do not possess angular, geminal, or spirane groupings on the carbon atoms which formerly were the carbon atoms of the carbonylenic double bond.

B. *Acetylenic dienophiles*

The above steric hindrance factors apply but little to the acetylenic dienophiles, since angular, geminal, or spirane groupings are not formed when these

substances add dienes. Addition to eneynes will give benzene derivatives directly, while addition of these dienophiles to diynes has not been attempted. The structure of the product from such a reaction, if reaction occurs, is indeed a matter for conjecture. Certain acetylenic derivatives, including acetylene itself, have been added to highly reactive dienes such as phencyclone (1,4-diphenyl-2,3-(o,o'-biphenylene)cyclopentadienone), but the most thoroughly studied derivatives have been those possessing *carbonylynic* groups, such as propiolic acid, acetylenedicarboxylic acid, and their methyl and ethyl esters. The adducts derived from the interaction of equimolecular quantites of acetylenic dienophile and *true* diene possess the carbonylenic grouping (if derived from the acetylenic acids) and are potentially able to add a second mole of diene. These primary adducts are dienophiles of Class B (see page 328) and are subject to the limitations of reaction rates of that class. The fact that these primary adducts may be isolated, usually in good yields, indicates that the second mole of diene is added with considerably greater difficulty than the first. This is reminiscent of the increasing difficulty in the progressive introduction of nitro groups into the aromatic nucleus.

It will be noted that the aliphatic dienophiles which add dienes readily are of the same type as those which add ammonia, amines, and hydrogen cyanide with ease.

C. *Non-carbonylenic dienophiles*

Dienophiles which possess neither the carbonylenic nor the carbonylynic group usually require elevated temperatures and occasionally an antioxidant (hydroquinone) to minimize polymerization of the diene. Temperatures as high as 200°C. may be required, but dienophiles with strongly acid groups attached to the carbon atoms of the double bond do not require conditions which are quite that drastic

Dimerization of dienes forms a special case wherein the diene acts as its own dienophile. This is perhaps the earliest known type of diene synthesis, and sufficient study has been made of the subject to warrant its being treated separately.

Table 1 summarizes the work accomplished with the addition of non-carbonylenic dienophiles to dienes. It will be noted that β-naphthol is capable of adding dienes, since its keto tautomer possesses the carbonylenic group.

Referring to table 1, it will be seen that secondary addition of cyclopentadiene to the normal adduct occurred in a number of cases, particularly those in which the reaction temperatures were higher than 100–110°C. Since the primary adducts are non-carbonylenic dienophiles, and since cyclopentadiene is a particularly reactive diene, addition to form secondary products is not surprising. The fact that considerable amounts of such products are formed indicates that the dienophilic activity of the dienophile employed in any one of these reactions is not much greater than that of the primary adduct with cyclopentadiene.

TABLE 1

Diene additions of non-carbonylenic dienophiles
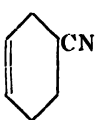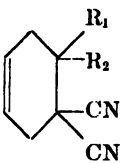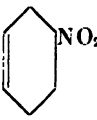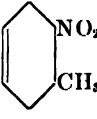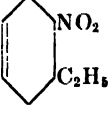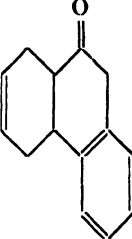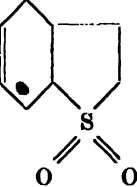
DIENE	DIENOPHILE	TEMPERA-TURE	PRODUCT	REFER-ENCE
		°C.		
Butadiene..........	Acrylonitrile			(371)
Butadiene, isoprene.	Methylene-malononi-trile de-rivatives			(382)
Butadiene..........	Nitro-ethylene	100–110		(20)
Butadiene........ .	1-Nitro-1-propene	100–110		(20)
Butadiene..........	1-Nitro-1-butene	100–110		(20)
Butadiene..........	β-Naphthol			(321)
Butadiene..........	Dihydrothio-phene dioxide	100–110		(20)
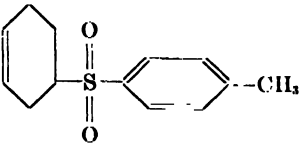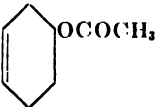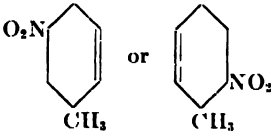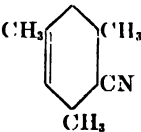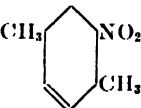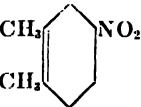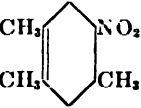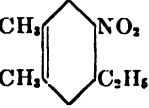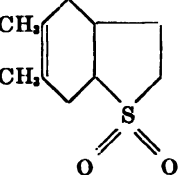
TABLE 1—*Continued*

DIENE	DIENOPHILE	TEMPERA-TURE	PRODUCT	REFER-ENCE
		°C.		
Butadiene	Vinyl-*p*-tolyl sulfone	100–110		(20)
Butadiene*	Vinyl acetate	180		(19)
Piperylene	Nitroethylene	100–110		(20)
1,3-Dimethylbutadiene	Crotononitrile			(246)
1,4-Dimethylbutadiene	Nitroethylene	100–110		(20)
2,3-Dimethylbutadiene	Nitroethylene	100–110		(20)
2,3-Dimethylbutadiene..	1-Nitro-1-propene	100–110		(20)
2,3-Dimethylbutadiene	1-Nitro-1-butene	100·110		(20)
2,3-Dimethylbutadiene	Dihydrothiophene dioxide	100·110		(20)
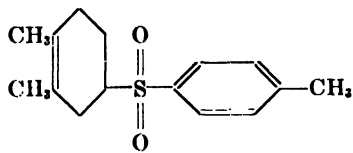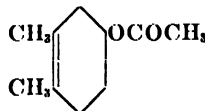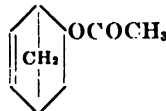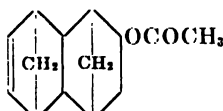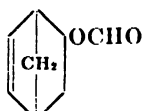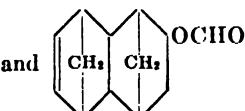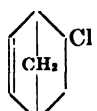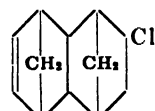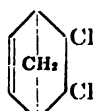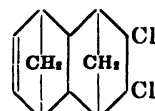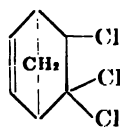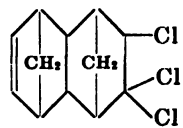
TABLE 1—*Continued*

DIENE	DIENOPHILE	TEMPERA-TURE °C.	PRODUCT	REFER-ENCE
2,3-Dimethylbu-tadiene	Vinyl-*p*-tolyl sulfone	100–110	[structure: CH₃, CH₃ substituted cyclohexene with SO₂–C₆H₄–CH₃ group]	(20)
2,3-Dimethylbu-tadiene	Vinyl acetate	180	[structure: CH₃, CH₃ substituted cyclohexene with OCOCH₃]	(19)
Cyclopentadiene†	Vinyl acetate	185–190	[structure: CH₂ bridged bicyclic with OCOCH₃] and [structure: CH₂ CH₂ tricyclic with OCOCH₃]	(19)
Cyclopentadiene†	Vinyl formate	180	[structure: CH₂ bridged bicyclic with OCHO] and [structure: CH₂ CH₂ tricyclic with OCHO]	(19)
Cyclopentadiene†	Vinyl chlo-ride	185	[structure: CH₂ bridged bicyclic with Cl] and [structure: CH₂ CH₂ tricyclic with Cl]	(19)
Cyclopentadiene†	1,2-Dichloro-ethylene	185	[structure: CH₂ bridged bicyclic with Cl, Cl] and [structure: CH₂ CH₂ tricyclic with Cl, Cl]	(19)
Cyclopentadiene†	Trichloro-ethylene	185	[structure: CH₂ bridged bicyclic with Cl, Cl, Cl] and [structure: CH₂ CH₂ tricyclic with Cl, Cl, Cl]	(19)
Cyclopentadiene‡	Nitroethyl-ene	100–110	[structure: CH₂ bridged bicyclic with NO₂]	(20)

TABLE 1—*Continued*
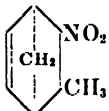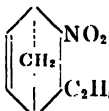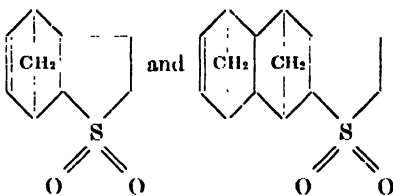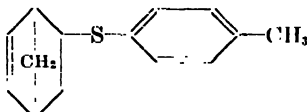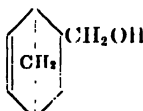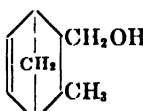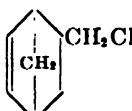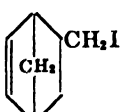
DIENE	DIENOPHILE	TEMPERA-TURE	PRODUCT	REFER-ENCE
		°C.		
Cyclopentadiene ...	1-Nitro-1-propene	100–110	[bicyclic structure with CH_2, NO_2, CH_3]	(20)
Cyclopentadiene ...	1-Nitro-1-butene	100–110	[bicyclic structure with CH_2, NO_2, C_2H_5]	(20)
Cyclopentadiene† ..	Dihydrothio-phene dioxide	180	[bicyclic structure with CH_2, S, O, O] and [bicyclic structure with CH_2 CH_2, ethyl, S, O, O]	(20)
Cyclopentadiene ...	Vinyl-*p*-tolyl sulfide	100	[bicyclic structure with CH_2, S—C$_6$H$_4$—CH_3]	(20)
Cyclopentadiene ...	Allyl alcohol	175–180	[bicyclic structure with CH_2, CH_2OH]	(40)
Cyclopentadiene ...	Crotyl alco-hol	175 180	[bicyclic structure with CH_2, CH_2OH, CH_3]	(40)
Cyclopentadiene ...	Allyl chloride	175–180	[bicyclic structure with CH_2, CH_2Cl]	(40)
Cyclopentadiene ...	Allyl bromide	175–180	[bicyclic structure with CH_2, CH_2Br]	(40)
Cyclopentadiene ...	Allyl iodide	100	[bicyclic structure with CH_2, CH_2I]	(40)

TABLE 1—*Continued*

DIENE	DIENOPHILE	TEMPERATURE °C.	PRODUCT	REFERENCE
Cyclopentadiene§ ..	Allylamine	175–180	[bicyclic structure] CH_2NH_2, CH_2	(40)
Cyclopentadiene ...	Crotononitrile		[bicyclic structure] CN, CH_2, CH_3	(246)
Cyclopentadiene† ..	Vinylacetonitrile	175–180	[bicyclic structure] CH_2CN, CH_2 and [structure] CH_2 CH_2 CH_2CN	(40)
Cyclopentadiene ...	Vinylacetic acid	175–180	[bicyclic structure] CH_2COOH, CH_2	(40)
Cyclopentadiene ...	Allyl isothiocyanate	175–180	[bicyclic structure] CH_2, $CH_2N{=}C{=}S$	(40)
Cyclopentadiene ...	Eugenol	175–180	[bicyclic structure] CH_2—CH_2—[benzene ring] OH, OCH_3	(40)
1,1,2-Trimethyl-cyclopentadiene¶.	Vinyl acetate	235–240	CH_3 [bicyclic structure] C CH_3 CH_3 $OCOCH_3$ + CH_3 [bicyclic structure] C CH_3 CH_3 $OCOCH_3$	(44)

TABLE 1—*Concluded*

DIENE	DIENOPHILE	TEMPERA-TURE	PRODUCT	REFER-ENCE
		°C.		
Methyl β-cam-phylate..........	Vinyl acetate	230	or	(44)
Tetraphenylcyclo-pentadienone.....	Benzonitrile	Reflux	+ CO	(181)
1,3-Cyclohexadiene.	Vinyl acetate	180		(19)
Anthracene........	Vinyl acetate	180		(19)
Anthracene.	Allyl alcohol	210–220		(40)
Anthracene...... ..	Indene	200–210		(291)

* Product is mainly 4-vinylcyclohexene, formed by dimerization of butadiene.

† The second product results from the addition of cyclopentadiene to the first product.

‡ Catalytic reduction of the adduct gave a nitro compound which yielded norbornylamine on reduction with zinc dust and acetic acid.

§ This adduct undergoes ring enlargement on treatment with nitrous acid, yielding 1,4-endomethylene-2-cyclohepten-6-ol.

¶ The *dl*-dehydrobornyl acetate was reduced and the product degraded to camphor.

D. Ketenes

Ketene, $H_2C{=}C{=}O$, bears the same relationship to the carbonylenic dienophiles as the allenes bear to the conjugated dienes. Addition of dienes to the ketenes does not occur according to the diene synthesis. In a number of cases, 1,2-addition of dienes to ketenes does occur to form fused-ring derivatives of cyclobutanone. This reaction differs in no essential respect (Staudinger) from the reactions of ketenes with monoölefinic compounds, for these types also form fused-ring derivatives of cyclobutanone if the olefin itself is cyclic. Straight-chain olefins and diolefins form straight-chain cyclobutanone derivatives.

Cyclopentadiene has been reported to react with ketene (96), but this is disputed by Smith and his students (336). Brooks and Wilbert (96) obtained a cyclobutanone derivative, in which the location of the double bond is uncertain. The compound may have either structure I or structure II.
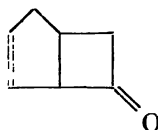
Diphenylketene and cyclopentadiene react at room temperature to yield the diphenyl derivative of I, according to Smith (336); Farmer and Farooq (198) report the product to be the diphenyl derivative of II. Reaction at higher temperatures results in the addition of a second mole of diphenylketene during a period of nine days (336) to give either III or its isomer IV. 1,3-Cyclohexadiene (198) gives V. By way of comparison, cyclopentene (336) gives VI and cyclohexene (198) gives VII.
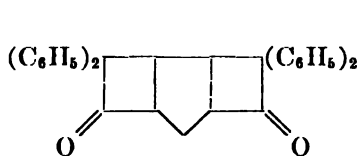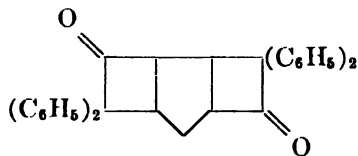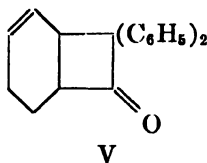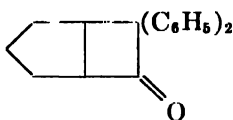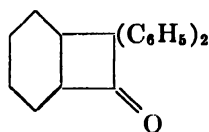
Ketene acetals may react in a unique manner with certain dienophiles. Condensation between 2 moles of ketene diacetal and 1 mole of maleic anhydride gives a diethoxydihydrophthalic anhydride (415):
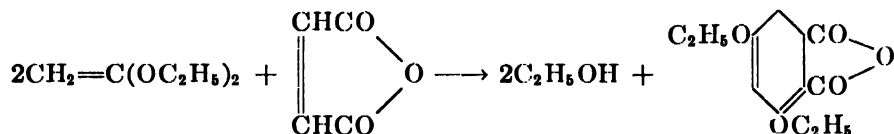
Dimethylmaleic anhydride does not react, and the reactions with p-benzoquinone and with benzalacetophenone proceed normally to give cyclobutane derivatives, but acetylenedicarboxylic ester yields 3,5-diethoxyphthalic ester (415).

E. Quinones as dienophiles

The majority of diene syntheses employing p-benzoquinone and α-naphthoquinone will be discussed in connection with the reactions of the various dienes and enynes. There are also a few other quinones mentioned elsewhere in this review, particularly with reference to the reactions of polynuclear hydrocarbons as dienes.

The quinones to be discussed include the true quinones— those which may be derived from aromatic compounds by direct oxidation —and those partially hydrogenated quinones which result from interaction of a diene and a true quinone. Of the various types of quinones and quinonoid substances, those derived from or benzologous with p-benzoquinone have been studied most extensively. Some work has been done with quinones derived from or benzologous with o-benzoquinones, and certain compounds such as the quinonoid form of 2,4-dinitrobenzeneazo-p-phenol have been shown to possess dienophilic properties.

(1) p-Quinones: There are definite limitations as to the types of quinones which will act as dienophiles by virtue of the quinonoid structure. While p-benzoquinone will add 2 moles of a diene, the addition of the second mole occurs with somewhat greater difficulty than the addition of the first. Fusion of a completely aromatic ring to the p-benzoquinone nucleus will completely suppress addition of the second mole of diene, although there is little or no effect on the addition rate for the first mole. α-Naphthoquinone and 1,4-anthraquinone therefore add but 1 mole of diene. Direct fusion of two completely aromatic rings to the p-benzoquinone nucleus will suppress all dienophilic properties. Thus 9,10-anthraquinone will not add dienes, but one finds that the two carbonyl groups activate the benzene rings sufficiently so that 9,10-anthraquinone will add a mole of dienophile (153). This is practically the sole case in which a lone benzene ring will add dienophiles, and the case is open to dispute (295). If the ring fused to the p-benzoquinone ring is also a p-benzoquinone ring, dienophilic properties of the fusion atoms are not destroyed, for naphthacenediquinone adds dienes readily.

Substituents in the p-benzoquinone ring other than fully aromatized rings exhibit a marked hindering effect on the speed of addition of dienes, and often suppress reaction entirely. Addition of dienes to such quinones would result in the formation of adducts possessing angular groups. This is analogous to the effect of substituents attached to the ethylenic carbon atoms of aliphatic dienophiles, which exhibit a less marked hindering effect on the reaction speed, and which also result in the formation of angular or geminal groups and, in one or two cases, spiranes. An exception is observed when the substituent is a group which promotes the entry of an ethylenic compound into the diene reaction, notably the carbonyl group. Groups (such as halogens or hydroxyl) which

can be easily eliminated from the adduct usually have but little hindering effect on the addition.

Despite the slowness of the additions observed with quinones possessing substituents attached to the carbon atoms of the carbonylenic double bond, Fieser is most optimistic concerning the possible uses of such quinones for the preparation of compounds related to sterols. This is due, no doubt, to the fact that other methods of synthesizing the sterol ring system are long and tedious and have low over-all yields.

In general, the extent to which quinones possess dienophilic properties (208) parallels their oxidation–reduction potentials. Quinones with high potentials possess greater additive power than those with lower potentials.

Certain of the foregoing statements are well illustrated by the addition of *p*-toluquinone to butadiene (103). One mole of butadiene may add to 1 mole of *p*-toluquinone to give one or both of two possible products, VIII and IX, the latter containing an angular methyl group. The fact that the product does

VIII   IX
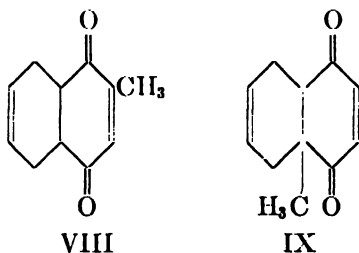
not contain such a group is to be anticipated. This addition occurs at temperatures well below 100°C., but the addition of the second mole of butadiene requires temperatures of 150°C. or higher. In spite of the fact that adducts tend to decompose into their generators on heating, the higher temperature is necessary in order to allow the formation of detectable quantities of adduct in reasonable time and also to minimize the polymerization of excess butadiene to 1-vinyl-3-cyclohexene and octahydrobiphenyl.

Addition of butadiene to *p*-xyloquinone must necessarily result in the formation of an adduct containing an angular methyl group. The hindering effect of two methyl groups is so great that Chang-Kong and Chin-Tsien (103) observed no addition at 150°C. with benzene as solvent. Adler (7) noted only 10 per cent addition under the same conditions. By using ethanol containing a trace of acetic acid as the reaction medium, Fieser and Seligman (222) were able to add a mole of butadiene to *p*-xyloquinone. 2,3-Dimethylbutadiene was also added to *p*-xyloquinone by the same technique.

A number of patents covering quinone additions (240–245, 247–250) are owned by the I. G. Farbenindustrie Aktiengesellschaft. Most of these were issued at or near the time of the appearance of the first paper by Diels and Alder. These patents cover various phases of the addition of typical dienes to *p*-benzoquinone, α-naphthoquinone, and to their immediate alkyl, hydroxyl, and halogen derivatives. One patent (245) covers the addition of 1 mole of a

diene to *p*-benzoquinone, followed by the addition of a second mole of the same
or a different diene to give a hydrogenated 9,10-anthraquinone. The patent
is sufficiently broad to cover the additions of tetralinquinone and the other
Bz-partially hydrogenated α-naphthoquinones.

Quinone additions appear to show steric and electronic hindrance effects to a
greater degree than other types of diene syntheses. In addition to steric
hindrance effects arising from substituents on the *p*-benzoquinone ring, decrease
of dienophilic activity is often noted when substituents are introduced into the
benzene rings which may be fused to the quinone ring. Progressive hydroxyla-
tion or acetoxylation of the benzene ring of α-naphthoquinone results in dimin-
ishing dienophilic activity. Furthermore, substitution in the 1- and 4-positions
of the conjugated diene may hinder progress of the diene reaction. If this
substituent is joined to both the 1- and the 4-positions so as to form a cyclic
diene, activity is usually enhanced. This is probably due to the conjugated
system being forced to remain in the (active) *cis*-configuration. Open-chain
dienes, such as butadiene, can revert to a *trans*-configuration easily, and the net
effect is to halve the concentration of reactive form as compared to cyclopenta-
diene or cyclohexadiene. Ring formation by bridging a carbonyl group between
the 1- and 4-positions of the butadienoid system leads to markedly enhanced
ability of the diene to add all types of dienophiles, as strikingly exhibited by
the derivatives of cyclopentadienone (*vide infra*). But simple alkyl groups,
as in piperylene or 2,4-hexadiene, usually lead to restricted addition of quinones.
Arbuzov and Spektermann (62) could obtain addition of only 1 mole of pipery-
lene or of 2,4-hexadiene to *p*-benzoquinone.

As indicated in the section on nitrogen heterocycles, the reactions of pyrroles
with quinones are abnormal. *p*-Benzoquinone adds 2 moles each of 2,5-
dimethylpyrrole, 2,3,4-trimethylpyrrole, and 2,4-dimethyl-3-ethylpyrrole (305)
to give compounds of the general structure shown in formula X. The by-product
in all three cases is quinhydrone, formed by oxidation of the initial product
(the *Bz*-tetrahydro derivative of X) by quinone. 2,5-Dibromo-*p*-benzoquinone
reacts similarly to give the *BQ*-2,5-dibromo derivatives of the compounds
indicated by the general structure X. Apparently the expected loss of hydrogen

X
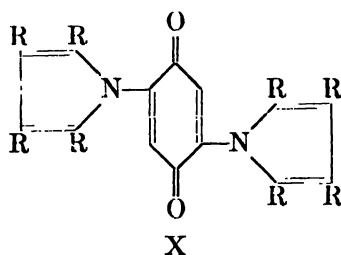
bromide from the initial product does not occur, and oxidation occurs preferen-
tially to give the *BQ*-2,5-dibromo derivatives. *p*-Toluquinone appears to react
with but 1 mole of 2,5-dimethylpyrrole, giving 2-(2,5-dimethyl-*N*-pyrryl)-5-
methyl-*p*-benzoquinone (305). This may be the 4-methyl isomer.

Toluquinone will add piperylene as well as butadiene (103, 222). A trace of hydrogen bromide will rearrange the adduct with 2,3-dimethylbutadiene (85, 103) into a hydroquinone (XI), while heating at 170°C. rearranges the same adduct to a mixture of XII and XIII:
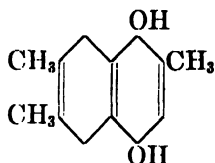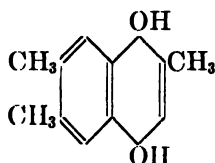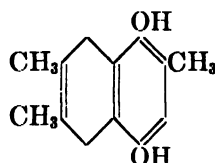
2,3-Diethoxybutadiene adds p-toluquinone (255) to give 2-methyl-6,7-diethoxy-5,5a,8,8a-tetrahydronaphthoquinone.

As indicated previously, p-xyloquinone will add dienes slowly (7) if at all (103), except under certain solvent conditions (222). The 10 per cent addition obtained by Adler (7) in the addition of butadiene to p-xyloquinone was the result of heating four mole proportions of diene with one of the quinone, the diene being in the form of a 20 per cent benzene solution. Heating was conducted at 160–170°C. for 10 hr.

p-Thymoquinone would be expected to behave in much the same manner as p-xyloquinone. It adds 2,3-dimethylbutadiene with considerable difficulty to give an oil which presumably has the structure shown in formula XIV. Piperylene is also added (222) to give an adduct assumed to be XV on the assumption that steric factors would prevent proximation of methyl groups. In the assign-

ment of structures XIV and XV it was also assumed that, because the methyl group is of smaller size than the isopropyl group, less difficulty would be encountered in the formation of an angular methyl group than in the formation of an angular isopropyl group.
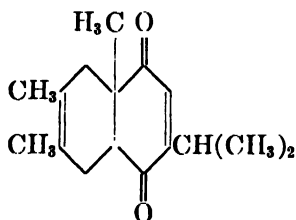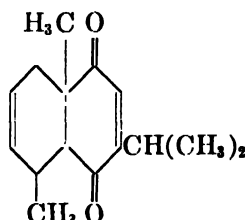
Phenyl-p-benzoquinone adds dienes in a manner similar to that of toluquinone, in that the product does not contain an angular group (85). At 100°C. addition occurs with 2,3-dimethylbutadiene and with cyclopentadiene, giving XVI and XVII, respectively. In contrast to the anthraquinone series, in which air oxidation of XVIII yields XIX, atmospheric oxidation of XVI gives XX in a reaction not unlike the formation of hydroxyjuglone from juglone.
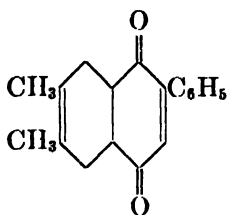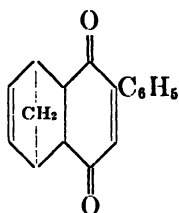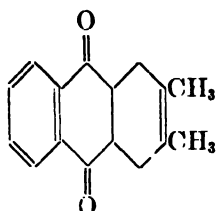
XVI   XVII   XVIII
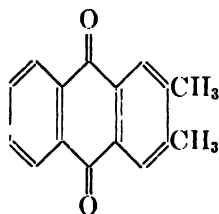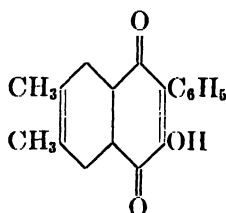
XIX   XX

1,4-Naphthoquinones exhibit the same types of steric hindrance effects as do the p-benzoquinones. α-Naphthoquinone itself (290) adds nearly all dienes easily. For example, it adds butadiene to give 1,1a,4,4a-tetrahydro-9,10-anthraquinone (136), 2,3-dimethylbutadiene to give 2,3-dimethyl-1,1a,4,4a-tetrahydro-9,10-anthraquinone (223), cyclopentadiene to give 1,4-endomethylene-1,1a,4,4a-tetrahydro-9,10-anthraquinone (153), and 1,3,5-hexatriene (99) to give what is believed to be 1-vinyl-1,1a,4,4a-tetrahydro-9,10-anthraquinone. Atmospheric oxidation of the hexatriene adduct gives 1-vinyl-9,10-anthraquinone.

Several alkylated α-naphthoquinones have been studied. All these have at least one methyl group in the 2-position. Because of this, addition to dienes occurs with some difficulty. 2,3-Dimethyl-1,4-naphthoquinone (221) exhibits a very slow reaction with 2.3-dimethylbutadiene, probably forming XXI. This product reverts into its generators when distilled *in vacuo*. 2,6-Dimethyl-1,4-naphthoquinone (221) reacts somewhat more readily than its isomer, giving XXII.
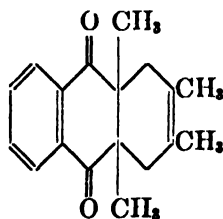
XXI   XXII
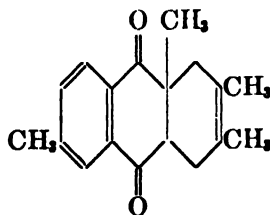
When α-naphthoquinone is substituted in the 2-position by the hydroxyl group, an adduct is formed which loses water readily to form a 1,4-dihydro-9,10-anthraquinone. Thus 2,3-dimethylbutadiene (208, 222) gives the 2,3-

dimethyl derivative. A similar effect is shown by the 2- and 3-halogenated
α-naphthoquinones, which lose hydrogen halide to yield more or less fully
aromatized 9,10-anthraquinones. Accordingly, butadiene and 2-chloro-1,4-
naphthoquinone (208) add to give XXIII, which loses hydrogen chloride easily
to give XXIV; and butadiene reacts with 2,3-dichloro-1,4-naphthoquinone
to give XXV, which loses 2 moles of hydrogen chloride to give anthraquinone.
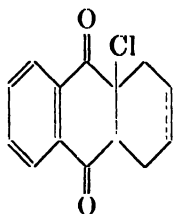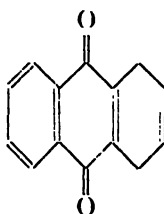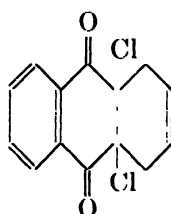
It was noted previously that progressive hydroxylation or acetoxylation of
the benzene nucleus of α-naphthoquinone led to decreased dienophilic activity.
Juglone (5-hydroxy-1,4-naphthoquinone) adds 2,3-dimethylbutadiene less
readily than does α-naphthoquinone (208). Naphthazarin (5,8-dihydroxy-1,4-
naphthoquinone) adds 2,4-hexadiene, piperylene, and alloöcimene (59) with
some difficulty; a 6-hr. heating period was necessary to obtain an 83 per cent
yield of adduct with 2,3-dimethylbutadiene, whereas only 20 min. heating was
necessary in order to obtain a 95 per cent yield of adduct from juglone and
2,3-dimethylbutadiene (208).

Naphthopurpurin may exist in two tautomeric forms, XXVI and XXVII:
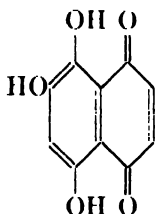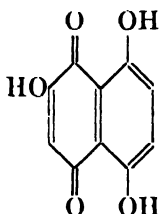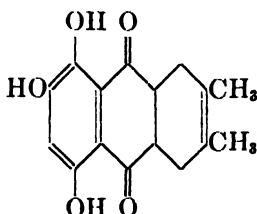
Since XXVII has an inhibiting group attached to the p-benzoquinone nucleus,
the structure of the naphthopurpurin adduct with 2,3-dimethylbutadiene
(208) may be predicted correctly as being XXVIII.

Juglone acetate (208) gives 5-acetoxy-1,1a,4,4a-tetrahydro-2,3-dimethyl-
9,10-anthraquinone with 2,3-dimethylbutadiene. Naphthazarin diacetate
adds piperylene to yield 1-methyl-5,8-diacetoxy-1,1a,4,4a-tetrahydro-9,10-
anthraquinone (175); isoprene gives the 2-methyl isomer. Isomerization of
these initial products occurs at the temperature (100°C.) employed to effect
these additions, so that the final product obtained is 1-(or 2)-methyl-5,8-
diacetoxy-1,2,3,4-tetrahydro-9,10-anthraquinone.

Heating naphthopurpurin triacetate with 2,3-dimethylbutadiene for a period

of 27 hr. is necessary in order to obtain the same yield of adduct that may be obtained by heating naphthazarin diacetate with the same diene for a period of only 3 hr. (208). A partially acetylated methylnaphthopurpurin, 2-methyl-8-hydroxy-5,6-diacetoxy-1,4-naphthoquinone (208), will add 2,3-dimethyl-butadiene, but only with considerable difficulty. The methyl ether of alkannin (307) is a derivative of naphthazarin and probably exists in two tautomeric forms, XXIX and XXX. It forms an adduct with 2,3-dimethylbutadiene, which is probably XXXI rather than XXXII.
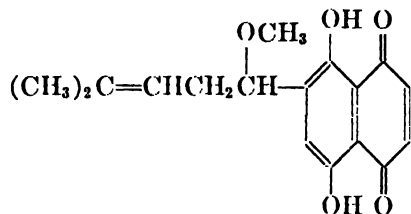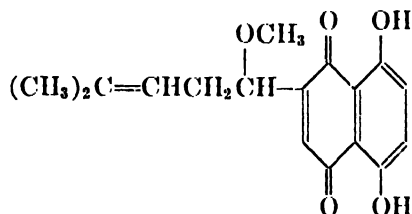
XXIX   XXX
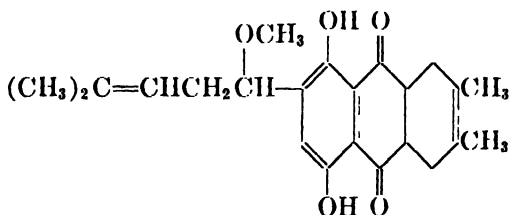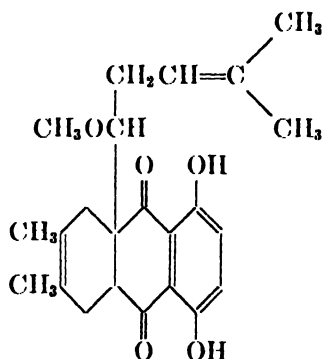
XXXI   XXXII

The only *p*-quinone derived from aromatic hydrocarbons of three or more fused rings which has been studied with respect to dienophilic properties (aside from 9,10-anthraquinone, which does not add dienes) is 9,10,11,12-naphthacenediquinone. No reports have been found concerning 1,4-anthraquinone, 1,4-naphthacenequinone, 1,4-phenanthrenequinone, or 9,10-naphtha-cenequinone. It is to be anticipated that all the 1,4-quinones will add dienes, and if the report of the addition of dienophiles to 9,10-anthraquinone can be confirmed, then it is likely that 9,10-naphthacenequinone will also add dieno-philes. The addition of 1 mole of anthracene to *p*-benzoquinone gives an adduct which is a derivative of 1,4-anthraquinone; this is 1a,4a,9,10-tetra-hydro-9,10-endo-(*o*-phenylene)-1,4-anthraquinone; it is easily oxidized to the 9,10-dihydro derivative. Both of these quinones add dienes.

9,10,11,12-Naphthacenediquinone (202, 203) adds butadiene and 2,3-dimethylbutadiene readily. This addition shows that the fusion of two *p*-benzoquinone rings to each other does not suppress addition of dienes to the

carbon atoms involved in the fusion, for the structure of the butadiene adduct
is as shown in formula XXXIII. A similar structure can be assigned to the
adduct with 2,3-dimethylbutadiene. This structure follows from the fact
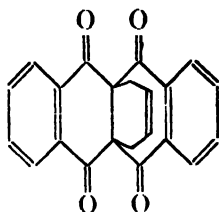
XXXIII

that, by atmospheric oxidation in alkaline solution, phthalic acid and 1,4-
dihydro-9,10-anthraquinone are formed.

(2) *Quinonoid compounds:* Among the nitrogenous analogs of *p*-benzoquinone
which add dienes in the diene synthesis (274) are quinone azine and various
derivatives of 2,4-dinitrobenzeneazo-*p*-phenol, which exist partly in the tauto-
meric form (XXXIV). This tautomeric form is the active form in the diene
synthesis. In the compounds investigated, R_1 is hydrogen, methyl, or bro-
mine, and R_2 is an aromatic ring which must possess not less than two nitro
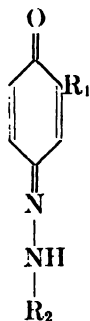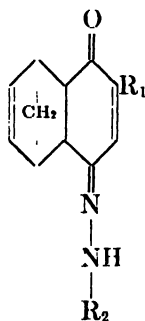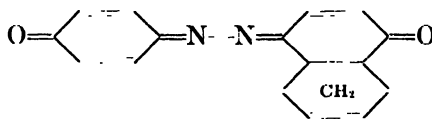
XXXIV   XXXV   XXXVI

groups. The adducts of compounds of this type with cyclopentadiene are of
the general structure XXXV. The cyclopentadiene adduct of quinone azine
has the structure shown in formula XXXVI.

(3) *o-Quinones:* The derivatives of *o*-benzoquinone have been investigated
recently with regard to their capacities to act as dienophiles. It has been found
that those ortho-quinones which possess a comparatively high degree of heat
stability will give adducts with dienes. *o*-Benzoquinone and β-naphthoquinone
are too unstable toward heat to give anything but tarry decomposition products,
but a number of substituted β-naphthoquinones and certain 1,2- and 3,4-
phenanthrenequinones have been shown to possess dienophilic properties.
It has been found that 3-substituted 1,2-naphthoquinones add dienes more
readily than do 2-substituted 1,4-naphthoquinones. Certain of these additions
are complete in 1 hr. at 100°C. (204, 221).

4-Substituted 1,2-naphthoquinones add dienes less readily than do their 3-substituted isomers. The addition of 2,3-dimethylbutadiene and 3-chloro-1,2-naphthoquinone is made complete by heating the components at 100°C. for 1 hr. (204, 221) in chloroform or methylene chloride solution; the product, 1a-chloro-1,1a,4,4a-tetrahydro-2,3-dimethyl-9,10-phenanthrenequinone, will lose hydrogen chloride fairly easily to give 1,4-dihydro-2,3-dimethyl-9,10-phenanthrenequinone. When the adduct is stored in a vacuum desiccator at 10°C., it decomposes to give a green-black amorphous mass. When this material is shaken in air with alcohol or ether, 2,3-dimethyl-9,10-phenanthrenequinone is produced (208).

4-Chloro-1,2-naphthoquinone adds to 2,3-dimethylbutadiene much less readily than does the 3-chloro isomer. The adduct, probably 4a-chloro-1,1a,4,4a-tetrahydro-2,3-dimethyl-9,10-phenanthrenequinone (208), was not isolated; it loses hydrogen chloride more readily than the 1a-chloro isomer, giving the same dihydrodimethylphenanthrenequinone.

3,4-Dichloro-1,2-naphthoquinone (208) adds 2,3-dimethylbutadiene when heated in chloroform solution for three days at 100°C. The adduct thereby obtained, 1a,4a-dichloro-1,1a,4,4a-tetrahydro-2,3-dimethyl-9,10-phenanthrenequinone, loses hydrogen chloride much less readily than does either of the two preceding adducts. When this does occur, the product is 2,3-dimethyl-9,10-phenanthrenequinone.

Care must be exercised in the preparation of adducts from the chloro-1,2-naphthoquinones, for traces of alcohol are especially deleterious. For this reason medicinal chloroform cannot be used as solvent. Other impurities in the materials used likewise have a deleterious effect on the progress of the reaction, and highly purified materials are required in order to assure good results.

An interesting sequence of reactions may be observed in the addition reaction of 3-chloro-1,2-naphthoquinone (209) and 2,3-dimethylbutadiene. 3-Bromo-1,2-naphthoquinone acts in a similar manner. The halogenated quinone is red; when it is heated with the diene, the color fades to yellow. This is the color of the 1a-halo-1,1a,4,4a-tetrahydro-2,3-dimethyl-9,10-phenanthrenequinone. On further heating, especially in direct sunlight, the red color reappears. Introduction of a second mole of 2,3-dimethylbutadiene, followed by further heating, causes a second fading of the color to yellow. The cause of this sequence of color changes is shown in the skeleton reactions:

(red)   (yellow)

(red)   (yellow)
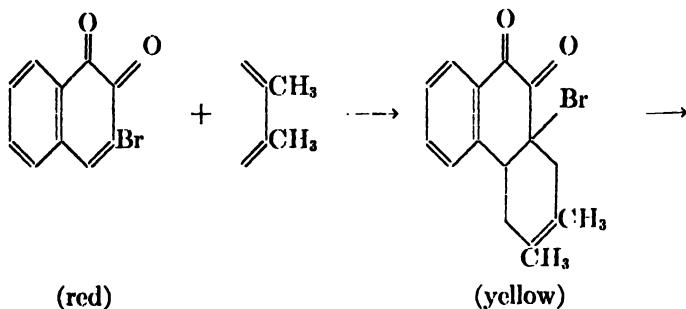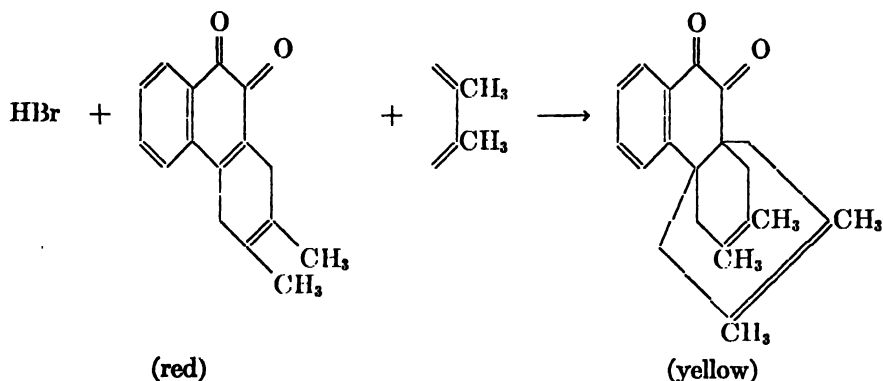
The adduct with 2 moles of 2,3-dimethylbutadiene usually loses a mole of the diene in preference to undergoing other reactions. Attempted formation of an oxime results in the loss of a mole of 2,3-dimethylbutadiene and formation of the dioxime of 2,3-dimethyl-1,4-dihydro-9,10-phenanthrenequinone. Pyrolysis in the presence of a mild oxidizing agent results in loss of 2,3-dimethylbutadiene and formation of 2,3-dimethyl-9,10-phenanthrenequinone.

6-Bromo-1,2-naphthoquinone (208) adds 2,3-dimethylbutadiene to give a product which is probably 6-bromo-2,3-dimethyl-1,1a,4,4a-tetrahydro-9,10-phenanthrenequinone.

Although 3,7-dimethyl-1,2-naphthoquinone adds dienes less readily than does 3-chloro-1,2-naphthoquinone, it adds a number of dienes which are not added by 2-methyl-1,4-naphthoquinone (204, 208, 221). A period of three days is required for addition of this quinone to 2,3-dimethylbutadiene by heating in alcoholic solution at 100–105°C., and less drastic conditions result in no addition. The product, 1a,2,3,7-tetramethyl-1,1a,4,4a-tetrahydro-9,10-phenanthrenequinone, is of importance in that it contains an angular methyl group.

In the α-naphthoquinone series it was found that progressive hydroxylation of the benzene ring resulted in decreasing dienophilic activity. The same is true of the β-naphthoquinone series. No reaction was observed (208) between 2,3-dimethylbutadiene and either 6- or 7-hydroxy-1,2-naphthoquinone.

4-Benzyl-1,2-naphthoquinone adds 2,3-dimethylbutadiene in a slow reaction (221) to give an adduct containing an angular benzyl group; the adduct is 1,1a,4,4a-tetrahydro-2,3-dimethyl-4a-benzyl-9,10-phenanthrenequinone.

4-(1,2-Naphthoquinonyl)malonic ester may be capable of isomerization into a 1,4-quinone structure (221):
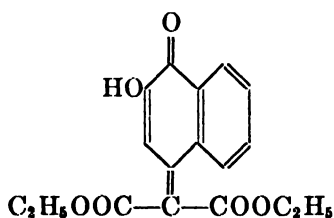
The compound adds 2,3-dimethylbutadiene, but Fieser appears to be reluctant to commit himself as to the structure of the adduct. The adduct may be derived from either the 1,4- or the 1,2-quinonoid structure. One may draw a tentative opinion from the fact that forced addition is usually required to obtain adducts of 4-substituted 1,2-ortho-quinones, and also from the fact that a hydroxyl group attached to the carbonylenic doubly bound carbon atoms does not greatly suppress dienophilic property. This would lead to the opinion that addition would tend to occur with the 1,4-quinonoid form rather than with the 1,2-form. If this be so, then the adduct should lose water on heating, and the product thus formed should be a 1,4-dihydro-2,3-dimethyl-9-methylene-anthrone derivative, decarboxylation and suitable dehydrogenation of which should give the methyleneanthrone itself.

9,10-Phenanthrenequinone does not add dienophiles, and it is also indifferent to dienes. Certain derivatives of 1,2- and 3,4-phenanthrenequinones have been examined by Fieser and Dunn (210); the adducts obtained were identified by degradation to chrysenequinones and benzophenanthrenequinones. The adduct of 2-bromo-3,4-phenanthrenequinone with 2,3-dimethylbutadiene was oxidized to 8,9-dimethyl-5,6-chrysenequinone, hydrogen bromide being eliminated in the first step of the degradation. The yield was 90 per cent on the basis of the generators. 3-Bromo-1,2-phenanthrenequinone gave with dimethylbutadiene an adduct which was oxidized with chromic acid to give 6,7-dimethyl-3,4-benz-9,10-phenanthrenequinone in an over-all yield of 58 per cent, based on the generators. By using butadiene, 3,4-benz-9,10-phenanthrenequinone was prepared from 3-bromo-1,2-phenanthrenequinone. It was found that 1,2-phenanthrenequinone would add 2,3-dimethylbutadiene, but at a slower rate than did the 3-bromo derivative. The latter was easily prepared by direct bromination of 1,2-phenanthrenequinone.

The courses of these syntheses with 2-bromo-3,4-phenanthrenequinone and with 3-bromo-1,2-phenanthrenequinone are given in skeleton equations (A and B) below:
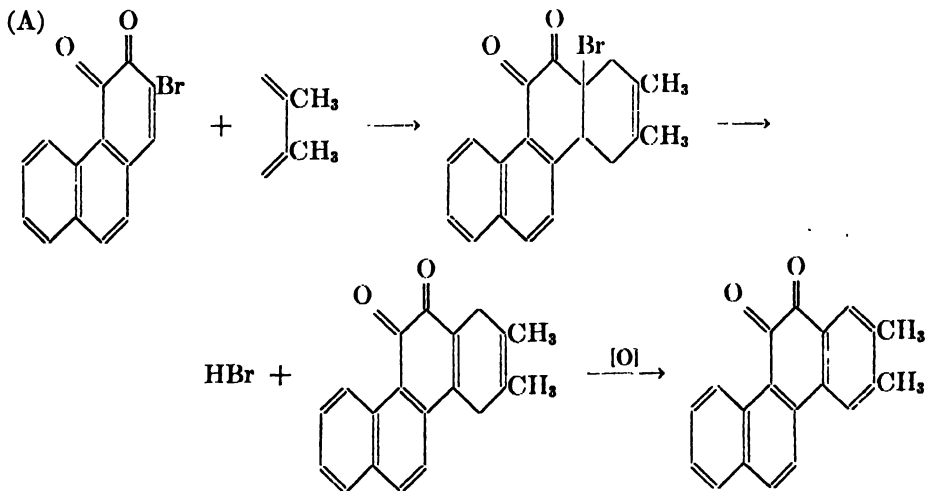
(B)
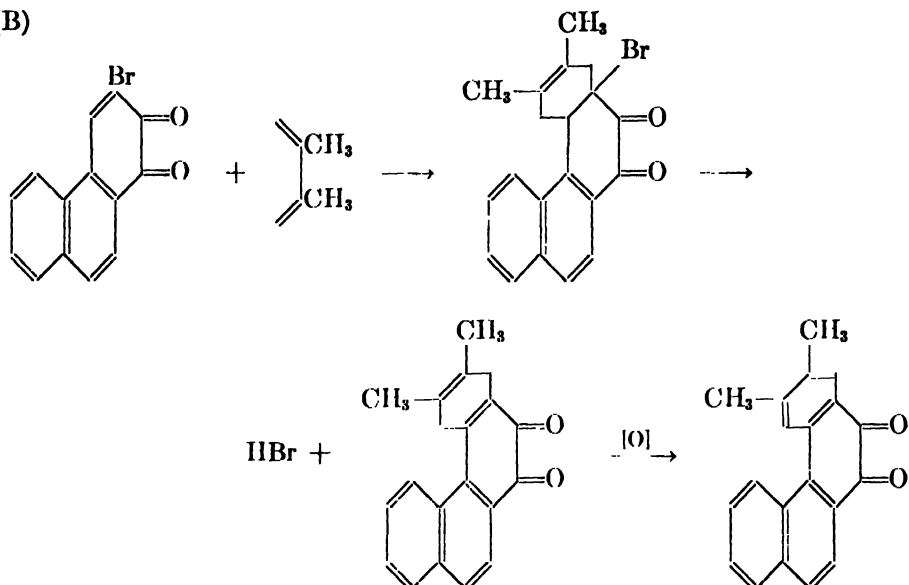
IV. DIENES: BUTADIENE AND SIMPLE DERIVATIVES

A. Simple derivatives of butadiene

The parent hydrocarbon, butadiene, reacts readily with acrolein (104, 105, 136, 144), crotonaldehyde (144), maleic anhydride (136), p-benzoquinone (23, 293), α-naphthoquinone (136), and many other dienophiles to give adducts of formulas which may be anticipated from the general rules for adduct structures which were given on page 320 of this review. The structures of the compounds formed are, respectively:
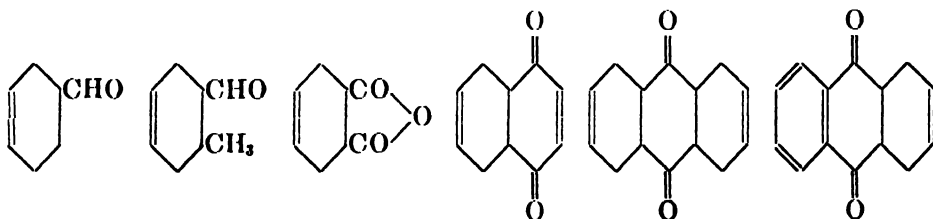
Piperylene (2,4-pentadiene) reacts with maleic anhydride (144) and with acrolein (63). The product of the latter reaction is illustrative of many cases of adducts the structures of which are problematical. This is always the case when both diene and dienophile do not possess a symmetrical structure with respect to the conjugated system or to the carbonylenic double bond, as the case may be. If either the diene or the dienophile is symmetrical, then the product of a normal diene reaction is of known structure.

The unsymmetrical diene and dienophile, as represented by piperylene and acrolein, may react to give one or both of two possible products:

$$CH_3 \quad\quad CH_2 \atop \quad\quad \| \atop CHCHO$$
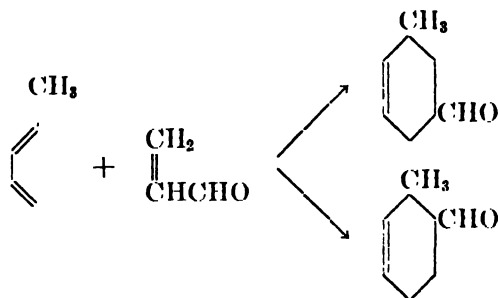
In this case, the structure of the product can be determined by dehydrogenation to the corresponding xylene. The boiling-point difference between *o*- and *m*-xylenes is not large; hence further confirmation would be desirable, such as oxidation of the xylene to the corresponding phthalic acid. Arbuzov (63) did not employ such a proof, but he gives the structure of the adduct of piperylene and acrolein as that of the meta-aldehyde. The structure of the adduct of maleic anhydride and piperylene may be deduced from the general rules for adduct formation.

There appears to be a substantial difference (309) in the rates of addition of maleic anhydride by the *cis*- and *trans*-isomers of piperylene. The analysis of a pure mixture of *cis*- and *trans*-piperylenes was attempted by Robey and his coworkers, who found that addition ceases between 65 and 78 per cent of completion. This was ascribed to differences in the rates of addition of dienophiles by the two isomers. Arguments for and against their belief that the unreactive form (which was isolated) is the *cis*-isomer may be found in the section dealing with the mechanism and stereochemistry of the diene synthesis (see page 496)[1].

[1] After this review had gone to press, Craig presented a paper before the 104th Meeting of the American Chemical Society at Buffalo, New York. In this paper, Craig showed quite convincingly that *trans*-piperylene (formed by gentle thermal decomposition of piperylene sulfone) adds maleic anhydride readily according to the general rules of diene syntheses. It was also shown that *cis*-piperylene will polymerize before it adds maleic anhydride, thus confirming previous observations. It must be considered, therefore, that the non-addition of maleic anhydride by *cis*-piperylene is a thoroughly established fact. Although cyclopentadiene is certainly of *cis*-configuration, it adds maleic anhydride with great avidity. A possible explanation for the apparent anomaly may be that while the butadienoid configuration of cyclopentadiene is forced to be *cis*, the butadienoid configuration of *cis*-piperylene may be either *cis* or *trans*, or a dynamic equilibrium between the two forms. If the methyl group of *cis*-piperylene exerts a steric hindrance effect upon the free rotation of the vinyl group around the bond linking carbon atoms 3 and 4 (considering *cis*-piperylene to be 2,4-pentadiene), then the butadienoid configuration of *cis*-piperylene may be largely or even exclusively a *trans*-butadienoid configuration at ordinary temperatures. Temperatures required to produce appreciable amounts of the *cis*-butadienoid form or of *trans*-piperylene may be as high as or higher than those required to induce polymerization under the acidic conditions employed (owing to the acid character of maleic anhydride). This question of steric control of the proportions of *cis*- and *trans*-butadienoid forms of a given 1,3-butadiene derivative is deserving of much further study.

Care must be taken in distinguishing between *cis-* and *trans*-isomers of a diene such as piperylene, and *cis-* and *trans*-butadienoid systems. Each isomer of piperylene may exist in both *cis-* and *trans*-butadienoid forms, which probably exist in dynamic equilibrium with each other. Thus *cis*-piperylene exists in *cis-* and *trans*-forms which are in dynamic equilibrium with each other, owing to free rotation about the single bond joining the 2- and 3-carbon atoms of the butadienoid system. In a *cis–trans*-butadienoid system such as this, in which the forms are spontaneously interconvertible, the existence of such a system may be disregarded for all practical purposes.[1]

The purest sample of 3,6-dihydrophthalic acid ever made is claimed by Diels and Alder, who prepared it by the addition of acetylenedicarboxylic acid to butadiene in dioxane solution (11). This preparation had a melting point nearly 13°C. higher than the preparation of von Baeyer.

Isoprene reacts with maleic anhydride (144), *p*-benzoquinone (153), and also with itself in dimerization and trimerization reactions (136, 275, 345, and 349) which differ sharply from its polymerization reactions. This dimerization reaction will be considered more fully in a later section (see page 430), but it will be of interest to note here that it and other dimerization reactions (except those of sorbic acid and the cyclopentadienones) are examples of additions which show that the dienophile need not contain double bonds of the carbonylenic type.

The reaction of isoprene with *p*-benzoquinone is entirely analogous to the reaction of butadiene with this dienophile. The first product of addition (I) may add another mole of isoprene to give either II or III:

    I   II   III
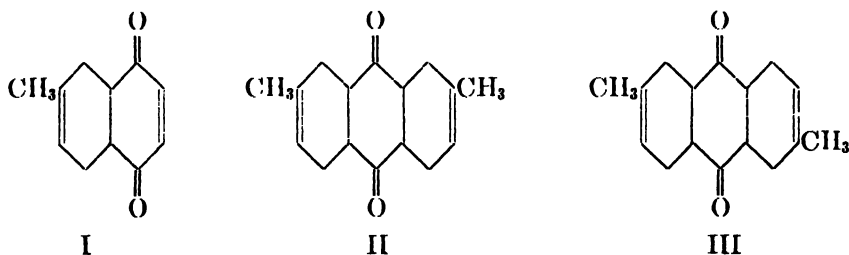
Actually, both products were obtained (153). Structures were proved by atmospheric oxidation to the corresponding dimethylanthraquinones.

2,4-Hexadiene reacts with crotonaldehyde, acrolein, and maleic anhydride (63, 144), but *p*-benzoquinone will add only 1 mole of the diene (62). Owing to the symmetrical nature of the diene, only one structure is possible for each of the adducts obtained thus. However, stereoisomerism is possible in the adducts. This phase of the structure of the adduct appears not to have been investigated.

1,3-Dimethylbutadiene is easily prepared by the method of the Saytzews (325), who obtained a hexadiene through the interaction of acetone, allyl bromide, and an alkali metal. The constitution of the product was not definitely established at the time, but the possibilities were limited to 1,3-dimethylbutadiene and 2-methyl-1,4-pentadiene. The latter substance does not possess

the conjugated system required of dienes which undergo the diene synthesis. Inasmuch as Diels and Alder (144) found that the diene reacted with maleic anhydride to give 3,5-dimethyl-1,2,3,6-tetrahydrophthalic anhydride, the structure of the Saytzew diene was established. The same diene was also obtained by pyrolysis of the phosphate of 2-methyl-2,4-diaminopentane (144) and also by dehydration of 2-methylpentene-2,4-glycol (144), as proved by the mutual identities of the adducts of maleic anhydride and also of crotonaldehyde with the products from each of the three sources.

2,3-Dimethylbutadiene has been well studied, both because of its symmetry and because of its ease of preparation. It reacts with 3-hexen-2,5-dione (227), 2-methylcyclopenten-3-one (93), maleic anhydride (144, 199), and acrolein (139, 144) to give adducts of anticipated structures. Of particular interest in this connection is that an angular methyl group is formed in the case of 2-methylcyclopenten-3-one:

2,3-Dimethylbutadiene   2-Methyl-
                             cyclopenten-
                             3-one
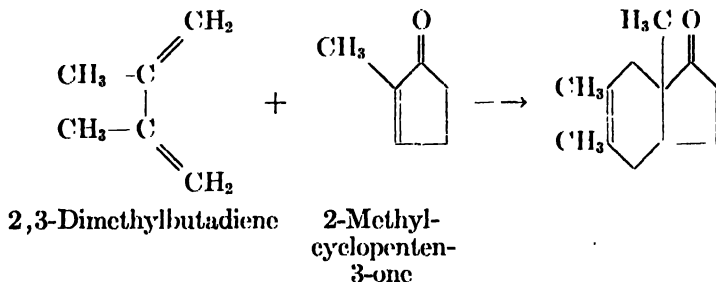
When dienophiles are employed which lead to the formation of angular, geminal, or spirane groups, the diene reaction often proceeds more slowly than if the potentially angular, etc., groups of the dienophile were absent. This subject was covered earlier in this review. Thus, the above reaction of 2-methyl-cyclopenten-3-one with 2,3-dimethylbutadiene is much slower than the reaction of butadiene with cyclopenten-3-one. Even the addition of diacetyl-ethylene is much more rapid than the addition of 1,2-diacetyl-1-propene (227). Where the mode of addition is optional, as in the addition of butadiene to p-toluquinone, the product does not contain an angular methyl group.

Having illustrated the simple diene syntheses by citing a number of typical examples, there should be no need of further elucidation of these simple types. For reference and informative purposes, however, there are listed in table 2 the simple butadiene derivatives which have been studied, together with the dienophile employed, the structure of the adduct, and the references to the literature.

With reference to table 2, it should be stated that in some cases the adduct structures are assumed, either by the author of this review or by the original investigators. Several cases will be noted in which addition fails to occur or else gives polymeric products. It may be that normal reaction will occur in a number of cases, provided the proper experimental conditions are determined and employed.[1]

TABLE 2

Diene syntheses with butadiene and simple derivatives
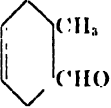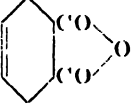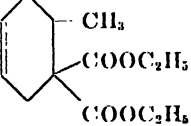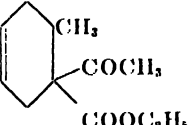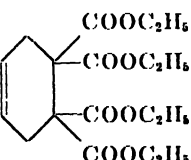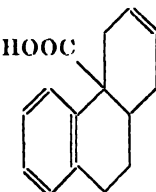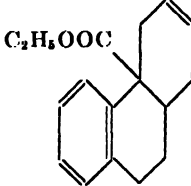
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Butadiene*.....	Acrolein	CHO	(104, 105, 136, 144)
Butadiene‡.. ...	Crotonaldehyde	CH₃ CHO	(105, 144)
Butadiene*.	Maleic anhydride	CO O CO	(136, 199)
Butadiene‡.. ...	Ethylidenemalonic ester	CH₃ COOC₂H₅ COOC₂H₅	(18)
Butadiene‡......	Ethylideneacetoacetic ester	CH₃ COCH₃ COOC₂H₅	(18)
Butadiene‡......	Ethylenetetracarboxylic ester	COOC₂H₅ COOC₂H₅ COOC₂H₅ COOC₂H₅	(18)
Butadiene‡......	3,4-Dihydro-1-naphthoic acid	HOOC	(219)
Butadiene‡......	3,4-Dihydro-1-naphthoic ester	C₂H₅OOC	(218)

TABLE 2 —*Continued*
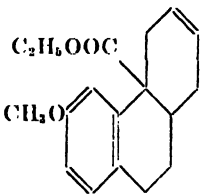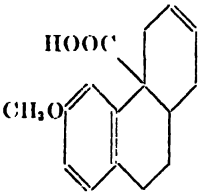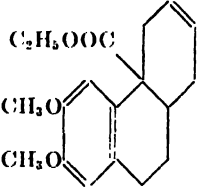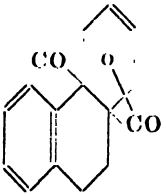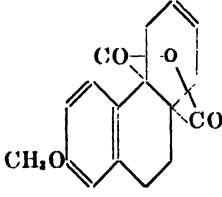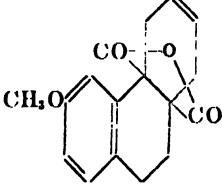
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Butadiene‡......	7-Methoxy-3,4-dihydro-1-naphthoic ester		(218)
Butadiene‡.......	7-Methoxy-3,4-dihydro-1-naphthoic acid		(219)
Butadiene‡.......	6,7-Dimethoxy-3,4-dihydro-1-naphthoic ester		(218)
Butadiene‡.......	3,4-Dihydro-1,2-naphthalic anhydride		(214, 216)
Butadiene‡.......	6-Methoxy-3,4-dihydro-1,2-naphthalic anhydride		(217)
Butadiene‡.......	7-Methoxy-3,4-dihydro-1,2-naphthalic anhydride		(217)

TABLE 2—*Continued*
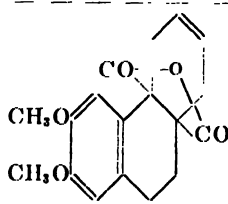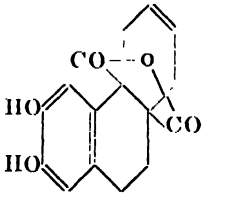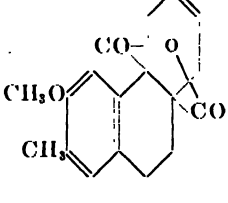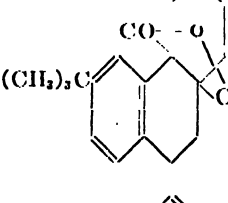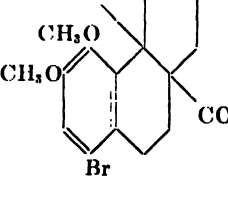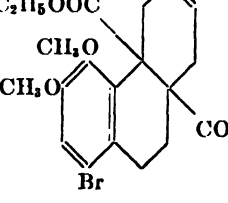
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Butadiene‡......	6,7-Dimethoxy-3,4-dihydro-1,2-naphthalic anhydride		(217)
Butadiene‡......	6,7-Dihydroxy-3,4-dihydro-1,2-naphthalic anhydride		(217)
Butadiene‡	6-Methyl-7-methoxy-3,4-dihydro-1,2-naphthalic anhydride		(217)
Butadiene‡... ..	7-tert-Butyl-3,4-dihydro-1,2-naphthalic anhydride		(220)
Butadiene‡......	7,8-Dimethoxy-5-bromo-3,4-dihydro-1,2-naphthalic acid		(218)
Butadiene‡......	7,8-Dimethoxy-5-bromo-3,4-dihydro-1,2-naphthalic ester		(218)

TABLE 2—*Continued*
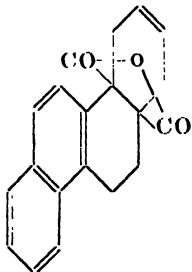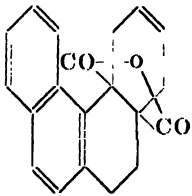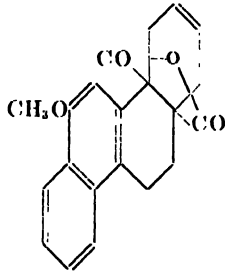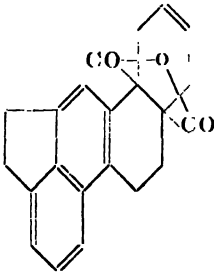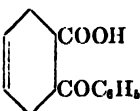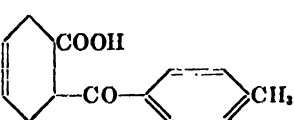
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Butadiene‡......	3,4-Dihydro-phenanthrene-1,2-dicarboxy-lic anhydride		(212, 213, 216)
Butadiene‡......	1,2-Dihydro-phenanthrene-3,4-dicarboxy-lic anhydride		(213, 216)
Butadiene‡......	9-Methoxy-3,4-dihydrophen-anthrene-1,2-dicarboxylic anhydride		(217)
Butadiene‡......	8,9-Ethylene-3,4-dihydrophen-anthrene-1,2-dicarboxylic anhydride		(213)
Butadiene‡......	β-Benzoylacrylic acid		(211, 215)
Butadiene‡......	β-p-Toluoylacry-lic acid		(215)

TABLE 2—*Continued*
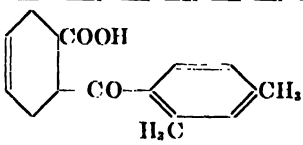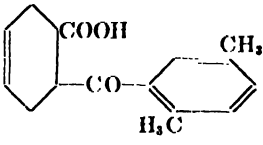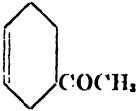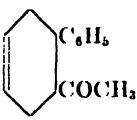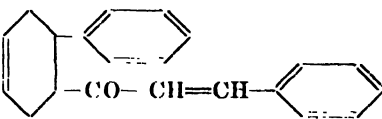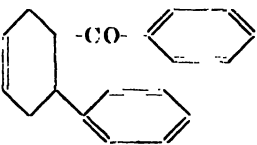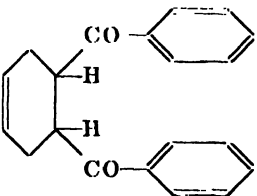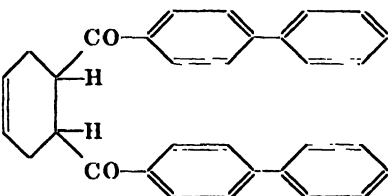
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Butadiene‡......	β-(2,4-Dimethyl-benzoyl)acrylic acid		(215)
Butadiene‡.......	β-(2,5-Dimethyl-benzoyl)acrylic acid		(215)
Butadiene‡......	Acetylethylene		(420)
Butadiene‡......	Benzalacetone		(297)
Butadiene.......	Ethylene	Cyclohexene	(411)
Butadiene‡......	Dibenzalacetone		(297)
Butadiene‡......	Benzalacetophe-none		(297)
Butadiene‡......	*trans*-1,2-Diben-zoylethylene		(3, 6)
Butadiene‡......	*trans*-1,2-Dixen-oylethylene		(4)

TABLE 2—*Continued*
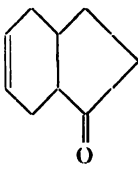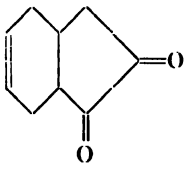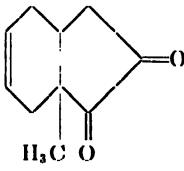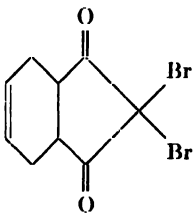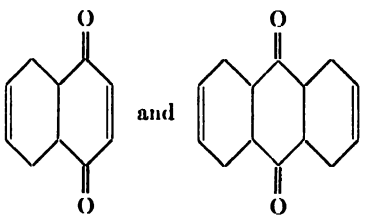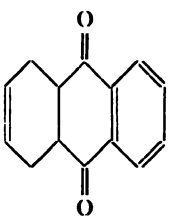
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Butadiene‡	1-Cyclopenten-3-one		(129)
Butadiene‡	1-Cyclopenten-3,4-dione		(134)
Butadiene‡	2-Methyl-1-cyclopenten-3,4-dione		(132)
Butadiene‡	4,4-Dibromo-1-cyclopenten-3,5-dione		(129)
Butadiene*	p-Benzoquinone	and	(23, 293)
Butadiene*	1,4-Naphthoquinone		(136)

TABLE 2—*Continued*
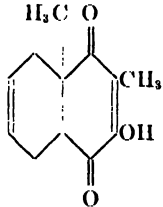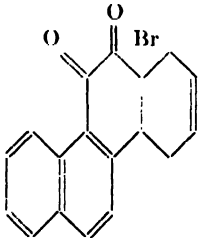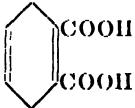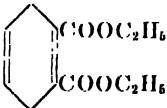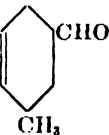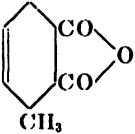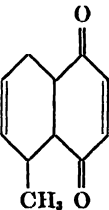
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Butadiene†	2,6-Dimethyl-3-hydroxy-1,4-benzoquinone		(132)
Butadiene‡	2-Bromo 3,4-phenanthrene-quinone		(210)
Butadiene‡	Acetylenedicar-boxylic acid	COOH COOH	(11)
Butadiene‡	Acetylenedicar-boxylic ester	COOC₂H₅ COOC₂H₅	(11)
Piperylene*	Acrolein	CHO CH₃	(63)
Piperylene‡	Maleic anhydride	CO O CO CH₃	(144)
Piperylene‡	p-Benzoquinone	CH₃ O	(62)

TABLE 2 - *Continued*
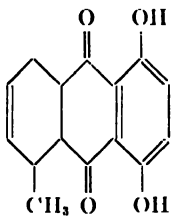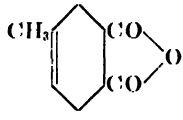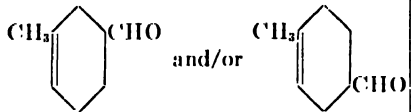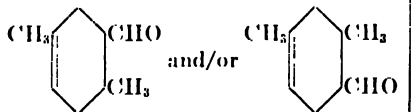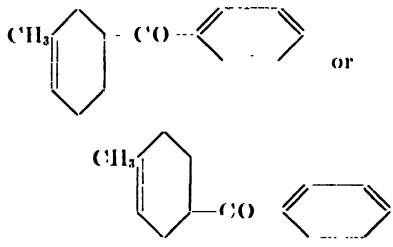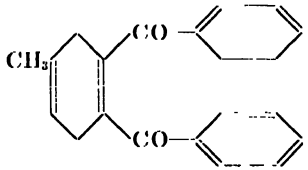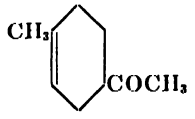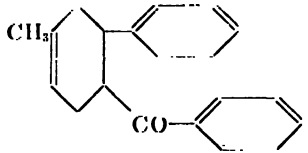
DIENE	DIENOPHILE	PRODUCT	REFER
Piperylene‡	Naphthazarin		(59)
Isoprene*	Maleic anhydride		(141)
Isoprene	Acrolein	and/or	(139)
Isoprene	Crotonaldehyde	and/or	(141)
Isoprene	Benzoylethylene	or	(47)
Isoprene‡	Dibenzoylacety-lene		(193)
Isoprene†	Acetylethylene		(120)
Isoprene†	Benzylideneace-tophenone		(297)

TABLE 2—*Continued*
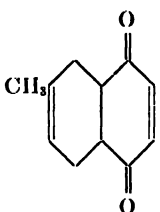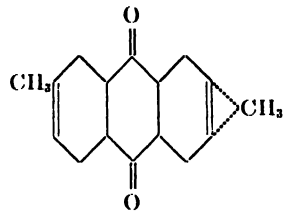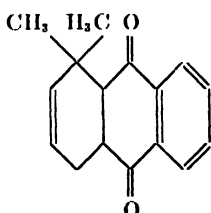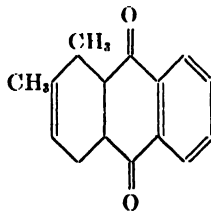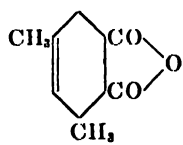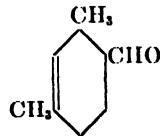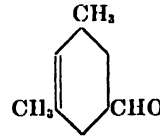
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Isoprene*	p-Benzoquinone	and both	(153, 195)
1,1-Dimethyl butadiene‡	Maleic anhydride	"Waxy polymeric anhydride"	(68, 390)
1,1-Dimethylbuta-diene‡	1,4-Naphtho-quinone		(224)
1,2-Dimethyl-butadiene‡	1,4-Naphtho-quinone		(223)
1,3-Dimethyl-butadiene‡	Maleic anhydride		(68, 105, 278, 390)
1,3-Dimethyl-butadiene†	Acrolein	or	(139, 331)

TABLE 2—*Continued*
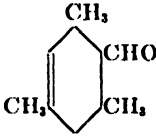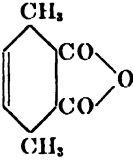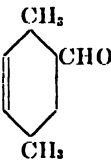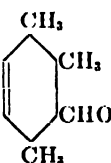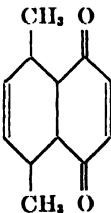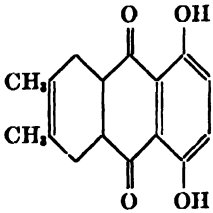
DIENE	DIENOPHILE	PRODUCT	REFERENCE
1,3-Dimethyl-butadiene†	Crotonaldehyde	CH₃ / CHO / CH₃ CH₃	(105, 139, 144)
1,4-Dimethyl-butadiene‡	Maleic anhydride	CH₃ / CO–O–CO / CH₃	(63, 283)
1,4-Dimethyl-butadiene‡	Acrolein	CH₃ / CHO / CH₃	(63)
1,4-Dimethyl-butadiene‡	Crotonaldehyde	CH₃ / CH₃ / CHO / CH₃	(105, 331)
1,4-Dimethyl-butadiene‡	p-Benzoquinone	CH₃ O / CH₃ O	(62)
1,4-Dimethyl-butadiene‡	Naphthazarin	O OH / CH₃ / CH₃ / O OH	(59)
2,3-Dimethyl-butadiene	Ethylene	1,2-Dimethylcyclohexene	(411)

TABLE 2—*Continued*
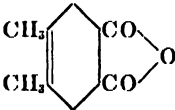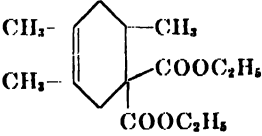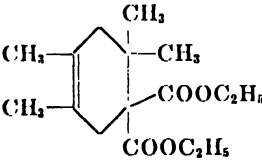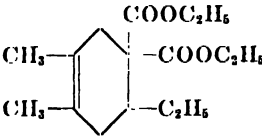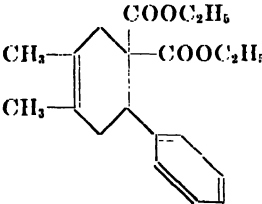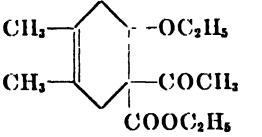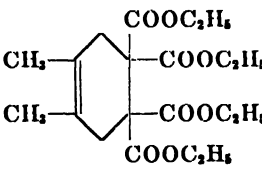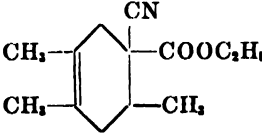
DIENE	DIENOPHILE	PRODUCT	REFERENCE
2,3-Dimethyl-butadiene‡.....	Maleic anhydride		(105, 199)
2,3-Dimethyl-butadiene‡.....	Ethylidenema-lonic ester		(18)
2,3-Dimethyl-butadiene‡.....	Isopropylidene-malonic ester		(18)
2,3-Dimethyl-butadiene‡.....	*n*-Propylidene-malonic ester		(18)
2,3-Dimethyl-butadiene‡.....	Benzylidenema-lonic ester		(18)
2,3-Dimethyl-butadiene‡.....	Ethoxymethy-leneacetoacetic ester		(18)
2,3-Dimethyl-butadiene‡.....	Ethylenetetra-carboxylic ester		(18)
2,3-Dimethyl-butadiene‡.....	Ethylidenecyano-acetic ester		(18)

TABLE 2—*Continued*

DIENE	DIENOPHILE	PRODUCT	REFERENCE
2,3-Dimethyl-butadiene‡.....	Benzylidenecy-anoacetic ester	CH_3 / CH_3 ring with CN, $COOC_2H_5$, phenyl	(18)
2,3-Dimethyl-butadiene‡.....	Ethylideneaceto-acetic ester	CH_3 / CH_3 ring with CH_3, $COCH_3$, $COOC_2H_5$	(18)
2,3-Dimethyl-butadiene‡.....	Benzylidenema-lononitrile	CH_3 / CH_3 ring with CN, CN, phenyl	(18)
2,3-Dimethyl-butadiene‡.....	β-Benzoylacrylic acid	CH_3 / CH_3 ring with CO-phenyl, COOH	(211, 215)
2,3-Dimethyl-butadiene‡.....	Methyl β-benz-oylacrylate	CH_3 / CH_3 ring with $COOCH_3$, phenyl	(47)
2,3-Dimethyl-butadiene‡.....	β-p-Toluylacrylic acid	CH_3 / CH_3 ring with COOH, phenyl-CH_3	(211, 215)
2,3-Dimethyl-butadiene‡.....	β-(2,4-Dimethyl-benzoyl)acrylic acid	CH_3 / CH_3 ring with COOH, dimethylphenyl (CH_3, CH_3)	(211, 215)

TABLE 2—*Continued*

DIENE	DIENOPHILE	PRODUCT	REFERENCE
2,3-Dimethyl-butadiene‡	β-(2,5-Dimethyl-benzoyl)acrylic acid		(211, 215)
2,3-Dimethyl-butadiene‡	3,4-Dihydro-1-naphthoic acid		(219)
2,3-Dimethyl-butadiene‡	7-Methoxy-3,4-dihydro-1-naphthoic acid		(219)
2,3-Dimethyl-butadiene‡	4-Bromo-7,8-di-methoxy-3,4-dihydro-1-naphthoic acid		(218)
2,3-Dimethyl-butadiene‡	4-Bromo-7,8-di-methoxy-3,4-dihydro-1-naphthoic ester		(218)
2,3-Dimethyl-butadiene‡	3,4-Dihydro-1,2-naphthalic an-hydride		(213, 214, 216)

TABLE 2—*Continued*
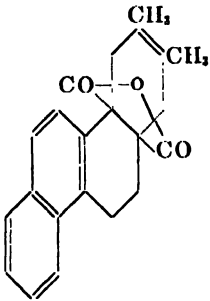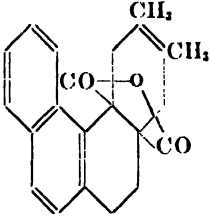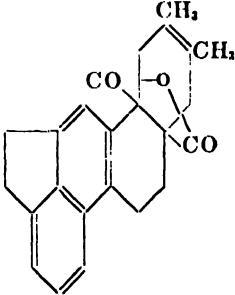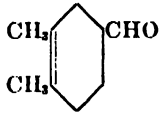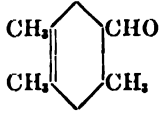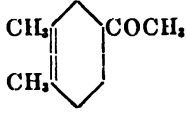
DIENE	DIENOPHILE	PRODUCT	REFERENCE
2,3-Dimethyl-butadiene‡.....	3,4-Dihydro-phenanthrene-1,2-dicarboxy-lic anhydride		(213, 216)
2,3-Dimethyl-butadiene‡.....	1,2-Dihydro-phenanthrene-3,4-dicarboxy-lic anhydride		(213, 216)
2,3-Dimethyl-butadiene‡.....	8,9-Ethylene-3,4-dihydrophen-anthrene-1,2-dicarboxylic anhydride		(209, 213)
2,3-Dimethyl-butadiene‡.....	Acrolein		(105, 139)
2,3-Dimethyl-butadiene‡.....	Crotonaldehyde		(139, 231)
2,3-Dimethyl-butadiene‡	Acetylethylene		(420)

TABLE 2—*Continued*
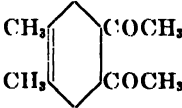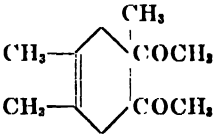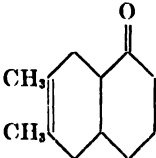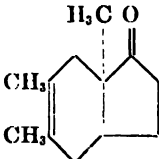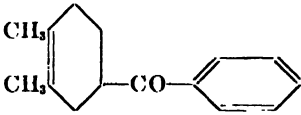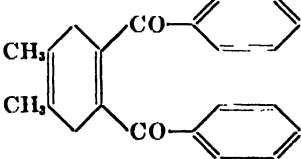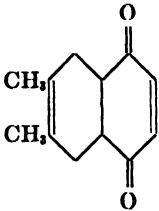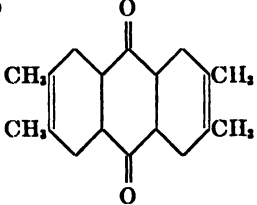
DIENE	DIENOPHILE	PRODUCT	REFERENCE
2,3-Dimethyl-butadiene‡.....	1,2-Diacetyl-ethylene		(227)
2,3-Dimethyl-butadiene‡....	1,2-Diacetyl-1-propene		(227)
2,3-Dimethyl-butadiene‡....	Cyclohexen-3-one		(76)
2,3-Dimethyl-butadiene‡.....	2-Methylcyclo-penten-3-one		(93)
2,3-Dimethyl-butadiene‡....	Benzoylethylene		(47)
2,3-Dimethyl-butadiene‡.....	Dibenzoylacety-lene		(193)
2,3-Dimethyl-butadiene‡.....	*p*-Benzoquinone		(23)

TABLE 2—*Continued*
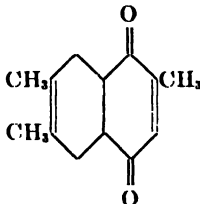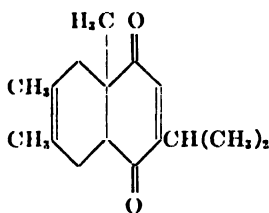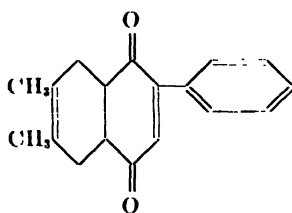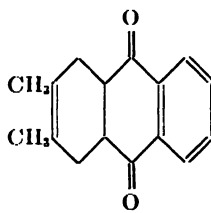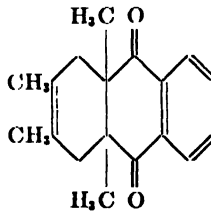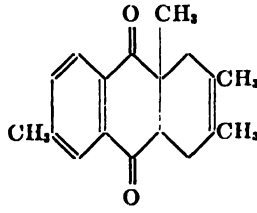
DIENE	DIENOPHILE	PRODUCT	REFERENCE
2,3-Dimethyl-butadiene‡.....	*p*-Toluquinone	(structure with CH₃, CH₃ and CH₃ substituents, two C=O)	(85, 103)
2,3-Dimethyl-butadiene‡.....	*p*-Thymoquinone	(structure with H₃C, CH₃, CH₃ and CH(CH₃)₂, two C=O)	(222)
2,3-Dimethyl-butadiene‡.....	Phenyl-*p*-benzo-quinone	(structure with CH₃, CH₃ and phenyl, two C=O)	(85)
2,3-Dimethyl-butadiene‡.....	α-Naphthoqui-none	(structure with CH₂, CH₂, two C=O)	(223)
2,3-Dimethyl-butadiene‡.....	2,3-Dimethyl-1,4-naphtho-quinone	(structure with H₃C, CH₃, CH₃, H₃C, two C=O)	(221)
2,3-Dimethyl-butadiene‡.....	2,6-Dimethyl-1,4-naphtho-quinone	(structure with CH₃, CH₃, CH₃, CH₃, two C=O)	(221)

TABLE 2—*Continued*
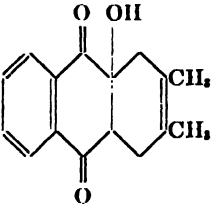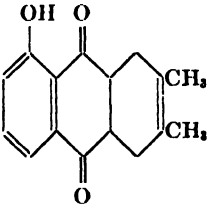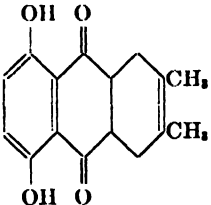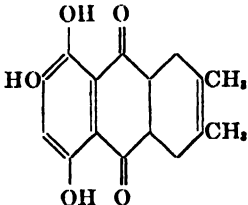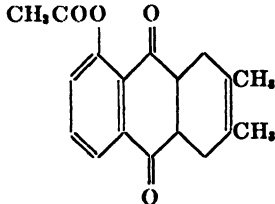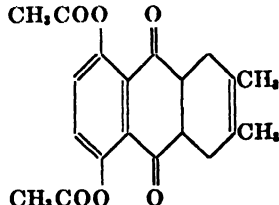
DIENE	DIENOPHILE	PRODUCT	REFERENCE
2,3-Dimethyl-butadiene‡	2-Hydroxy-1,4-naphthoquinone		(208, 222)
2,3-Dimethyl-butadiene‡	Juglone		(208)
2,3-Dimethyl-butadiene‡	Naphthazarin		(208)
2,3-Dimethyl-butadiene‡	Naphthopurpurin		(208)
2,3-Dimethyl-butadiene‡	Juglone acetate		(208)
2,3-Dimethyl-butadiene‡	Naphthazarin diacetate		(208)

TABLE 2—*Continued*
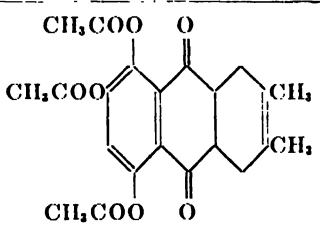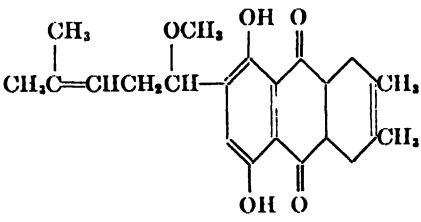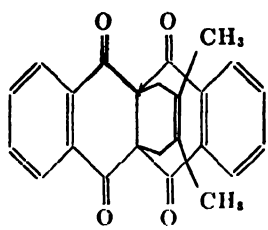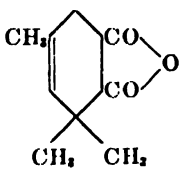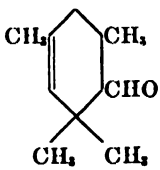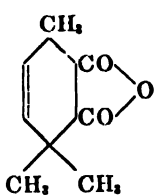
DIENE	DIENOPHILE	PRODUCT	REFERENCE
2,3-Dimethyl-butadiene‡.....	Naphthopurpurin triacetate		(208)
2,3-Dimethyl-butadiene‡.....	Alkannin methyl ether		(307)
2,3-Dimethyl-butadiene‡.....	Naphthacenedi-quinone		(202, 203)
1,1,3-Trimethyl-butadiene†.....	Maleic anhydride		(144)
1,1,3-Trimethyl-butadiene†.....	Crotonaldehyde		(144)
1,1,4-Trimethyl-butadiene‡.....	Maleic anhydride		(68)

TABLE 2—*Continued*
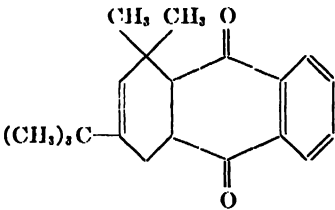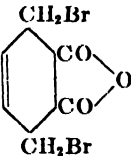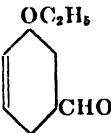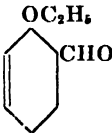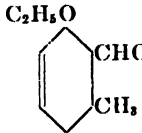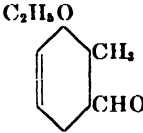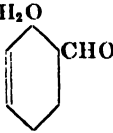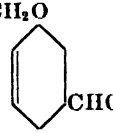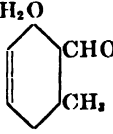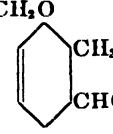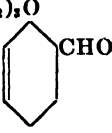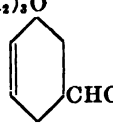
DIENE	DIENOPHILE	PRODUCT	REFERENCE
1-Isopropylbuta-diene........	Maleic anhydride	"Waxy polymeric adduct"	(68)
3-*tert*-Butyl-1,1-dimethylbuta-diene‡.........	α-Naphthoquin-one	CH_3 CH_3 O ... $(CH_3)_3C$ ... O	(224)
1,4-Di(bromo-methyl)buta-diene‡.........	Maleic anhydride	CH_2Br / CO–O–CO / CH_2Br	(137)
1-Ethoxybuta-diene†.........	Acrolein	OC_2H_5 ... CHO or OC_2H_5 ... CHO	(358)
1-Ethoxybuta-diene†.........	Crotonaldehyde	C_2H_5O ... CHO ... CH_3 or C_2H_5O ... CH_3 ... CHO	(358)
1-*n*-Propoxybuta-diene†.........	Acrolein	$C_2H_5CH_2O$ ... CHO or $C_2H_5CH_2O$ ... CHO	(358)
1-*n*-Propoxybuta-diene†.........	Crotonaldehyde	$C_2H_5CH_2O$ ... CHO ... CH_3 or $C_2H_5CH_2O$ ... CH_3 ... CHO	(358)
1-*n*-Butoxybuta-diene†.........	Acrolein	$CH_3(CH_2)_3O$ ... CHO or $CH_3(CH_2)_3O$ ... CHO	(358)

TABLE 2—*Continued*
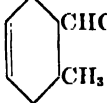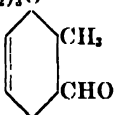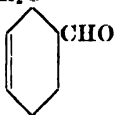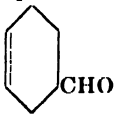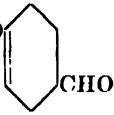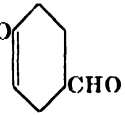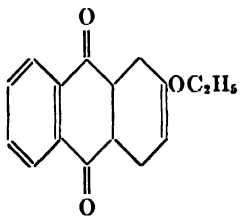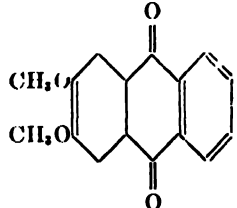
DIENE	DIENOPHILE	PRODUCT	REFERENCE
1-*n*-Butoxybuta-diene†	Crotonaldehyde	$CH_3(CH_2)_3O$ CHO or CH₃ (and) $CH_3(CH_2)_3O$ CH₃ CHO	(358)
1-Isobutoxybuta-diene†	Acrolein	$(CH_3)_2CHCH_2O$ CHO or $(CH_3)_2CHCH_2O$ CHO	(358)
2-Methoxybuta-diene†	Acrolein	CH_3O CHO	(419)
2-Ethoxybuta-diene†	Acrolein	C_2H_5O CHO	(419)
2-Ethoxybuta-diene†	α-Naphthoquin-one	O ... OC_2H_5 ... O	(402)
2,3-Dimethoxy-butadiene‡	α-Naphthoquin-one	O ... CH_3O CH_3O ... O	(255)

TABLE 2—*Continued*
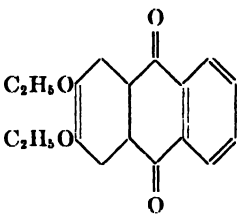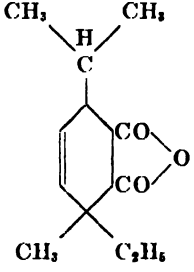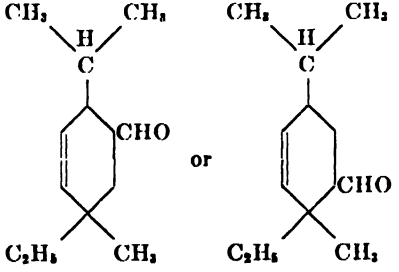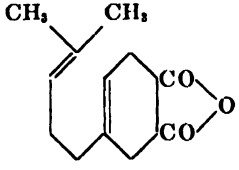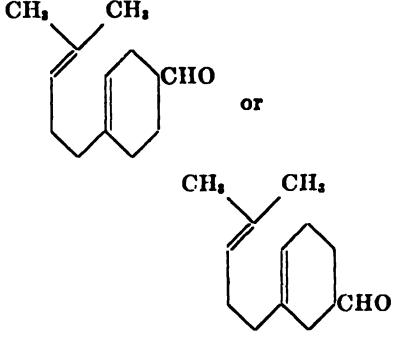
DIENE	DIENOPHILE	PRODUCT	REFERENCE
2,3-Diethoxy-butadiene‡	α-Naphthoquin-one		(255)
2,6-Dimethyl-3,5-octadiene‡	Maleic anhydride		(192)
2,6-Dimethyl-3,5-octadiene†	Acrolein		(192)
Myrcene‡	Maleic anhydride		(43, 144, 407)
Myrcene†	Acrolein		(139)

TABLE 2—*Continued*
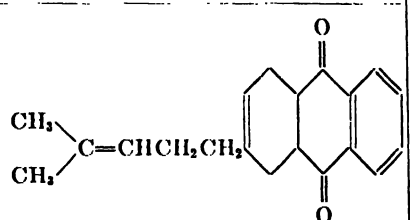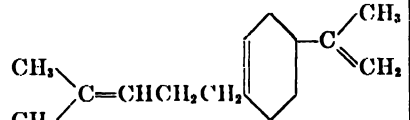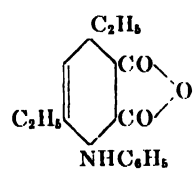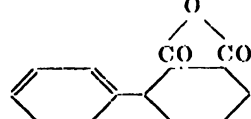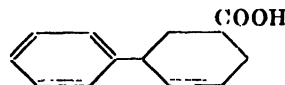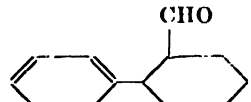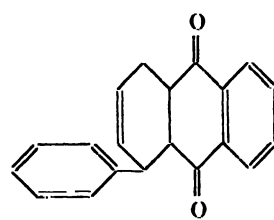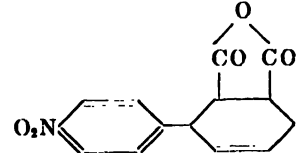
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Myrcene†	α-Naphthoquin-one		(224)
Myrcene†	Isoprene	or isomers	(315)
1,3-Diethyl-4-(*N*-anilino) buta-diene	Maleic anhydride		(423, 424)
1-Phenylbuta-diene‡	Maleic anhydride		(17, 152)
1-Phenylbuta-diene*	Acrylic acid	COOH	(277, 281)
1-Phenylbuta-diene*	Acrolein	CHO	(277, 281)
1-Phenylbuta-diene‡	α-Naphthoquin-one		(153)
1-*p*-Nitrophenyl-butadiene‡	Maleic anhydride		(88)

TABLE 2—*Continued*
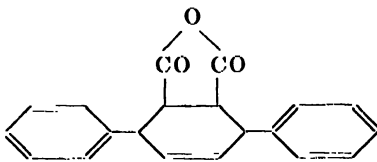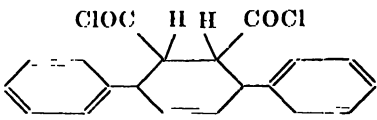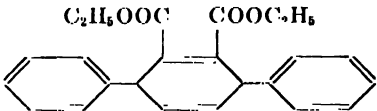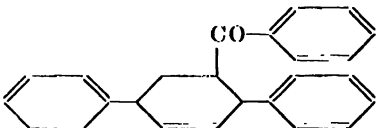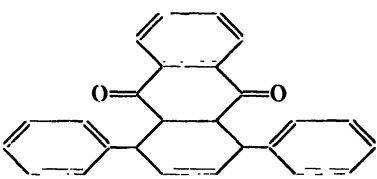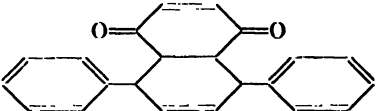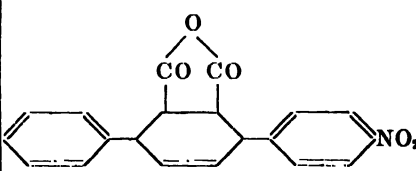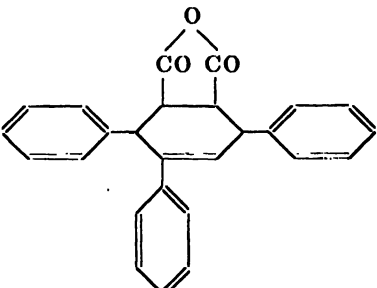
DIENE	DIENOPHILE	PRODUCT	REFERENCE
1,4-Diphenyl-butadiene‡....	Maleic anhydride		(273)
1,4-Diphenyl-butadiene‡.....	Fumaroyl chloride		(273)
1,4-Diphenyl-butadiene‡.....	Acetylenedicarboxylic ester		(288)
1,4-Diphenyl-butadiene‡.....	Benzoylethylene		(47)
1,4-Diphenylbutadiene‡........	α-Naphthoquinone		(425)
1,4-Diphenylbutadiene‡........	p-Benzoquinone		(425)
1-Phenyl-4-(p-nitrophenyl) butadiene‡........	Maleic anhydride		(88)
cis-1,2,4-Triphenylbutadiene‡........	Maleic anhydride		(87)

<div align="center">TABLE 2—Continued</div>
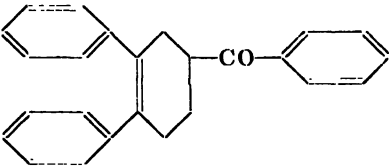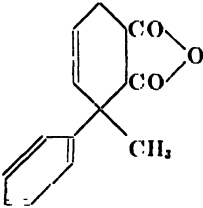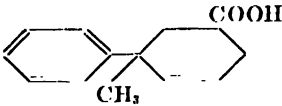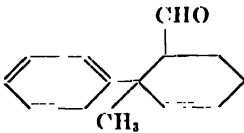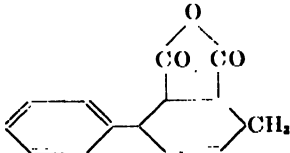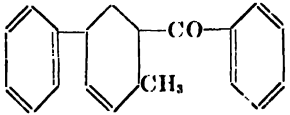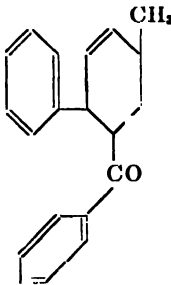
DIENE	DIENOPHILE	PRODUCT	REFERENCE
trans-1,2,4-Tri-phenylbutadiene	Maleic anhydride	No reaction	(87)
2,3-Diphenylbu-tadiene‡........	Benzoylethylene		(47)
1-Phenyl-1-methylbu-tadiene‡........	Maleic anhydride		(279)
1-Phenyl-1-meth-ylbutadiene† ..	Acrylic acid		(279)
1-Phenyl-1-meth-ylbutadiene* ..	Acrolein		(277, 279)
1-Phenyl-4-meth-ylbutadiene‡ ...	Maleic anhydride		(144)
1-Phenyl-4-meth-ylbutadiene† ..	Benzoylethylene	or	(47)

TABLE 2—*Continued*
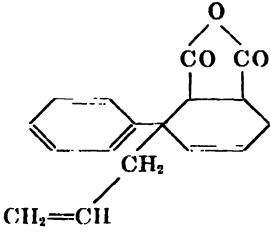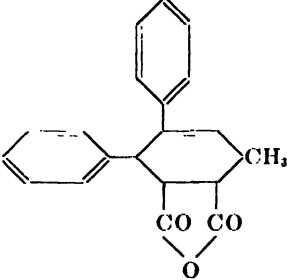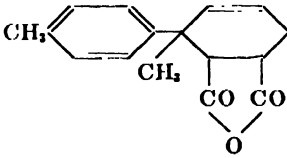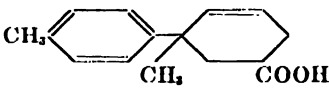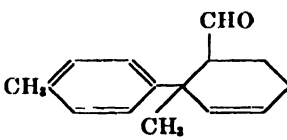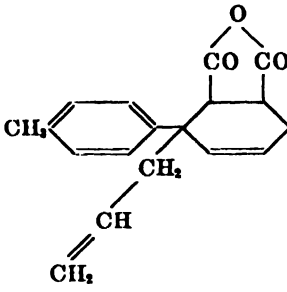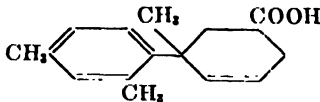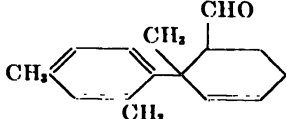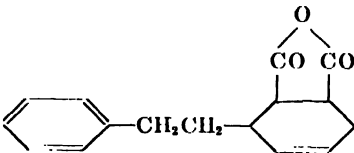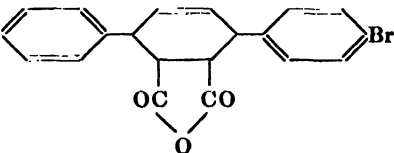
DIENE	DIENOPHILE	PRODUCT	REFERENCE
1-Phenyl-1-allyl-butadiene‡......	Maleic anhydride		(280)
1,2-Diphenyl-4-methylbu-tadiene‡........	Maleic anhydride		(87)
1-*p*-Tolyl-1-methylbu-tadiene‡........	Maleic anhydride		(279)
1-*p*-Tolyl-1-methylbu-tadiene†........	Acrylic acid		(279)
1-*p*-Tolyl-1-methylbu-tadiene†	Acrolein		(277, 279)
1-*p*-Tolyl-1-allyl-butadiene‡......	Maleic anhydride		(280)

TABLE 2—*Concluded*

DIENE	DIENOPHILE	PRODUCT	REFERENCE
1-(4-*m*-Xylyl)-1-methylbutadiene†........	Acrylic acid		(279)
1-(4-*m*-Xylyl)-1-methylbutadiene†........	Acrolein		(277, 278, 281)
1-(2-Phenylethyl)-butadiene‡......	Maleic anhydride		(122)
1-(2-Phenylethyl)-1-methylbutadiene.........	Maleic anhydride	Amorphous powder at 110 C.	(122)
1-(2-(*m*-Methoxyphenyl)ethyl)-butadiene.......	Maleic anhydride	No reaction	(122)
1,2,3,4-Tetraphenylbutadiene.........	Maleic anhydride	No reaction	(425)
1,4-Di(*p*-anisyl)-butadiene.......	Maleic anhydride	No reaction	(425)
1-Phenyl-4-*p*-bromophenylbutadiene.........	Maleic anhydride		(410)
1-(2-(*m*-Methoxyphenyl)ethyl)-butadiene.......	Acrolein	No reaction	(122)
1,4-Bis(*o*-biphenylene)butadiene	Maleic anhydride	No reaction	(346)

* Structure of adduct proved in literature cited.
† Structure of adduct assumed.
‡ Structure of adduct considered evident because only one structure is possible by the general rules (page 320) of adduct formation.

Referring again to table 2, the adduct of 1-phenyl-1-methylbutadiene and acrylic acid was found in two forms. Theoretically, one might obtain two acids, for it is theoretically possible for the carboxyl group to become located either ortho or meta to the geminal grouping. Each of these two acids should exist in two forms, depending on whether the carboxyl group is *cis* or *trans* with respect to the methyl (or the phenyl) group of the geminal system. Hence four acids are theoretically possible through the addition of acrylic acid to 1-phenyl-1-methylbutadiene. Furthermore, each of the four acids should be resolvable into *d*- and *l*-forms. The above assumes that the *cis*-form of cyclohexene is the only form capable of existence. Now the structure of the adduct resulting from the interaction of 1-phenyl-1-methylbutadiene and acrolein was proved. If the acrylic acid adducts have the formula given in table 2, then oxidation of the acrolein adducts should give one or both of the acids obtained by acrylic acid addition. Oxidation was accomplished by a Cannizzaro reaction (279), and two acids were produced. One of these was identical with an acid obtained by acrylic acid addition, but the other was not. Presuming that the acrolein is added to give a mixture of the *cis*- and the *trans*-forms of the compound given in table 2, then a logical conclusion is that acrylic acid adds to 1-phenyl-1-methylbutadiene to give a mixture of one of the ortho acids with one of the meta acids. While this explains the findings of Lehmann (279), it has not been proved conclusively. The case of 1-phenylbutadiene is related to this specific problem. Its acrolein adduct has the aldehyde group ortho to the geminal system, while its acrylic acid adduct has the carboxyl group meta to that system.

Parallel situations are found in the cases of the acrolein and acrylic acid adducts of 1-*p*-tolyl-1-methylbutadiene and of 1-(2,4-dimethylphenyl)-1-methylbutadiene, and may be amenable to the same explanation. Each forms one acrolein and two acrylic acid adducts. Two acids are formed upon oxidation of the acrolein adduct, only one of which is identical with one of the acrylic acid adducts. Structures of the acrolein adducts were not proved, however.

The structure of the product obtained from *p*-benzoquinone and 1-phenyl 1-methylbutadiene is assumed to be the oxidized adduct shown, because of the extensive reduction of excess quinone to hydroquinone and quinhydrone. The adducts of butadiene with *p*-benzoquinone are easily oxidized to naphtho- and anthra-quinones, the structures of which are those of 5,8-dihydro-1,4-naphthoquinone and 1,4,5,8-tetrahydro-9,10-anthraquinone; this may be accomplished in an alkaline medium at room temperature with atmospheric oxygen. It is logical, therefore, to assume that in the case of 1-phenyl-1-methylbutadiene and *p*-benzoquinone, the hydrogenated quinone ring of the original adduct is completely aromatized by the excess *p*-benzoquinone.

Addition of maleic anhydride to 1,4-diphenylbutadiene appeared to give four isomeric acids melting in the range 198° to 203°C. The form melting at 198°C. decomposed into its generators on distillation. From a stereochemical point of view, two anhydride adducts could be produced in which the phenyl groups are para and *cis* to each other, and one anhydride adduct could be produced

in which the phenyl groups are *trans* to each other. The two *cis*-forms and the one *trans*-form explain three of the four acids observed. The fourth acid may be formed by a change of one of the acids (all of which possess carboxyl groups *cis* to each other) into an acid in which the carboxyl groups are *trans* to each other. For reasons to be discussed later, it is not likely that the anhydride possessing *trans*-phenyl groups is formed in the diene synthesis; therefore it seems more likely that certain of the four acids are the result of isomerizations of the *cis*-phenyl-*cis*-acids which are presumed to be formed initially.

<div align="center">TABLE 3</div>

<div align="center">*Reaction of chlorinated dienes with dienophiles*</div>

DIENE	REACTION*	REFERENCE
1-Chloro-1,2-butadiene....	Negative	(101)
Chloroprene (2-chlorobutadiene)	Positive	(102)
3-Methylchloroprene	Positive	(121)
1-Alkylchloroprenes	Positive	(121, 254)
3,4-Dimethylchloroprene	Positive	(121)
2,3-Dichlorobutadiene	Positive	(89, 121)
1,2,3,5-Tetrachloro-2,4-pentadiene	Negative	(121)
1,3,4-Trichloro-2,4,5-hexatriene	Negative	(121)
3,4-Dichloro-1,2,4,5-hexatetraene	Negative	(121)
1-Chlorobutadiene (α-chloroprene)	Negative	(121)
4-Chloro-1,2,3,4-hexatetraene	Negative	(121)
1,4-Dichloro-2,3,5-hexatriene	Negative	(121)
1,2-Dichlorohexa-3-yne-5-ene	Negative	(121)
3,4-Dichloro-1,3,5-hexatriene	Negative	(121)
1,6-Dichloro-2,3,4-hexatriene	Negative	(121)
4-Chloro-1,2,3,5-hexatetraene	Negative	(121)
1-Chloromethylchloroprene	Positive	(202)
1-Bromomethylchloroprene	Positive	(201)
1-Chloro-5-methoxy-2,3-pentadiene	Negative	(403, 404)
1-Methoxy-3-chloro-2,4-pentadiene	Positive	(403, 404)

* In the eight cases in which addition occurred, the formulas of the products were in accord with those postulated by application of the general rules of adduct formation

B. Halogenated dienes

Some work has been done on halogenated dienes, particularly by Carothers and his coworkers. With respect to the ability of these dienes to add maleic anhydride or α-naphthoquinone, the following generalizations may be drawn: (a) Dienes of the structure Cl—C=C—C=C or C=C(Cl)—C(Cl)=C do not add dienophiles. (b) Dienes of the structure C=C(Cl)—C=C, in the absence of other chlorine atoms in the molecule, usually add dienophiles as well as do the parent hydrocarbons.

Table 3 lists chlorodienes which were tested with respect to their ability to add 1,4-naphthoquinone or maleic anhydride. In those cases where reaction occurs, the structure of the product is that predicted by the general rules of

adduct formation.   It will be noted that one of these compounds is an allene, while certain others combine the structures of allenes and conjugated dienes.

The conclusion of Carothers was that when the diene reaction is used as a test for conjugation, it is conclusive only when positive.   Even so, this may not be strictly true unless reaction is observed at or near room temperature, particularly in the cases of terpenes and sterols.   Further, the diene synthesis will not detect *trans*-butadienoid configurations as such.   In the cases of terpenes, certain additions occurred when the "diene" contained an isolated-double-bond system or a lone double bond; in one case, the "diene" was a fully saturated compound.   All additions in these cases were conducted at elevated temperatures and the same adduct could, in certain instances, be obtained from several different "dienes," which is conclusive proof of isomerization in one or more stages of the addition.   These materials did not react readily at room temperature, although the end products postulated for the isomerization of the materials prior to undergoing the diene synthesis reacted readily at room temperature.

C. Allenes

Dienes containing the grouping C=C=C do not react with dienophiles, provided (a) isomerization to a conjugated system does not occur under the conditions of the experiment, and (b) the compound under investigation does not contain a conjugated system in addition to the allene system, as in the skeletons C=C=C—C=C and C=C=C—C—C=C—C=C.   Certain of these compounds were investigated by Carothers and reported in table 3.   The only other studies made were those of 1-cyclohexyl-2,3-pentadiene, which does not add maleic anhydride (2), and of 1-phenyl-1,2-butadiene, which adds neither maleic anhydride nor 1,4-naphthoquinone (1).

D. Enynes

As indicated in the earlier portions of this review, only a few enynes have been studied.   Most of those studied belong to the dienyne class.   The field is being opened up, however, by Lewis and Eleanore Butz and their coworkers. At this writing their latest paper is to be read at the 102nd Meeting of the American Chemical Society, and it will deal with enynes in the diene synthesis.

The addition of 2,5-dimethylhexa-1,5-dien-3-yne (100) and maleic anhydride proceeds, probably in two steps, to give a reduced naphthalenetetracarboxylic dianhydride:

(1)

$$(2)$$
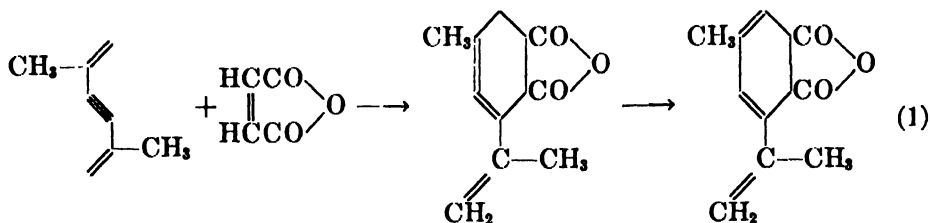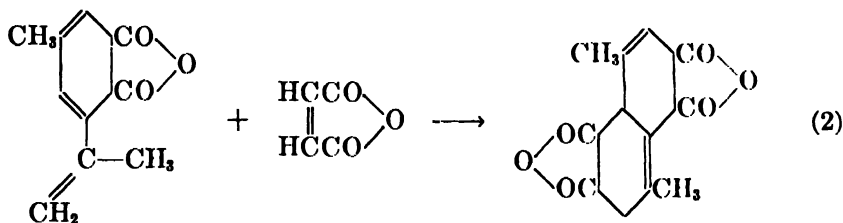
The mechanism given is that proposed by Butz; however, it seems unnecessary and indeed undesirable to postulate the isomerization of the first adduct before addition of the second mole of maleic anhydride. The author is not aware of the certainty of the locations of the double bonds in the final product as claimed by Butz. If isomerization must occur before the second mole of dienophile is added, then the substance obtained would be a mixture of the product indicated by Butz with the final product indicated immediately below:
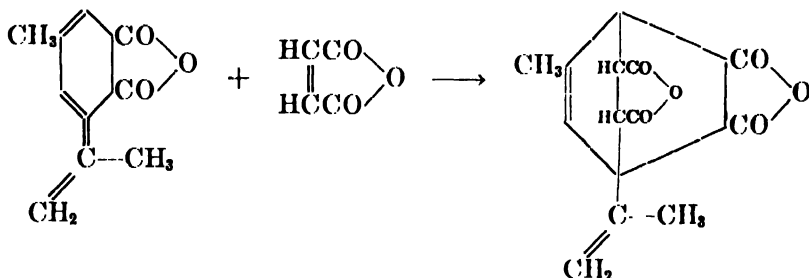
That this conclusion is not unreasonable may be seen when it is pointed out that 1,3-cyclohexadienes are slightly more active in the diene synthesis than are open-chain dienes. If isomerization does not occur prior to addition of the second mole of maleic anhydride, the product would be that indicated below, barring subsequent isomerization:
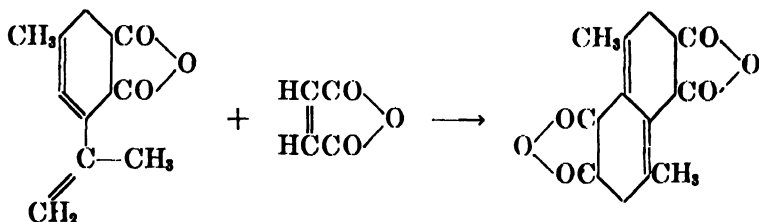
A recent paper by Joshel, Butz, and Feldman (412) describes the diene syntheses accomplished with di(1-cyclohexenyl)acetylene and 1-cyclohexenyl(2-methyl-1-cyclohexenyl)acetylene, each of which adds 2 moles of maleic anhydride. The formula of the product is given as that which might be expected if no rearrangement of double bonds occurs between the additions of the first and the second moles of maleic anhydride:

(R = II or CH₃)
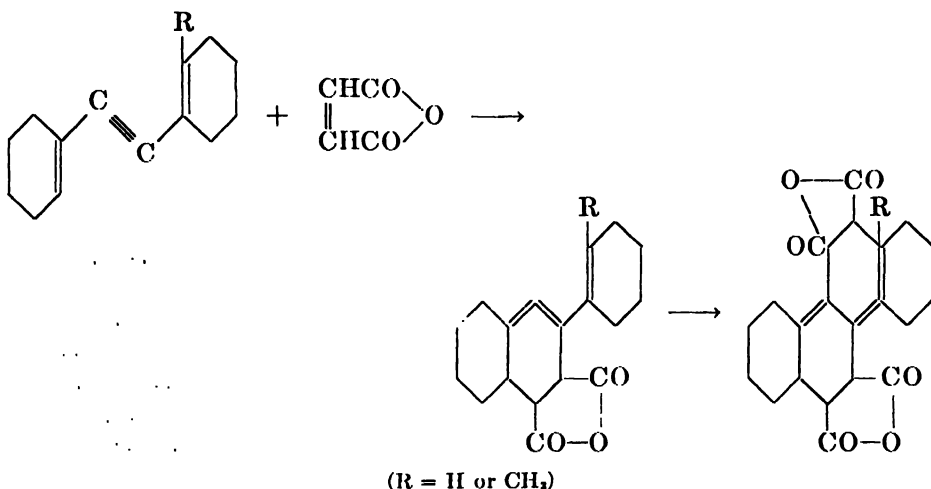
Butz and Joshel (398) have been able to synthesize compounds containing the sterol-ring structure by employing 1-cyclohexenyl-1-cyclopentenylacetylene in the diene synthesis. With maleic anhydride, the reaction appears to proceed as follows:
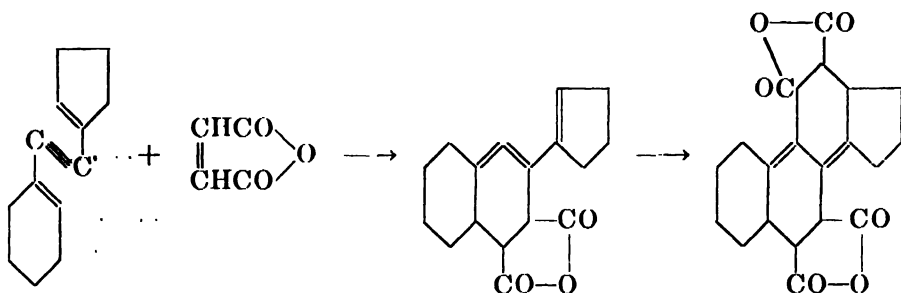
Dimethyl and diethyl fumarates have been added (399) to the above two cyclic dienynes to give adducts of structures similar to those with maleic anhydride.

The yields of adducts from these diene syntheses are not usually very high, since carbon atoms 1 and 4 of the vinylacetylene residue are further apart than in dienes. This is because acetylene is a straight-line molecule, while ethylene is more angular. In vinylacetylene and butadiene a comparison may be drawn. The inference is that proximity of carbon atoms 1 and 4 favors the diene synthesis:
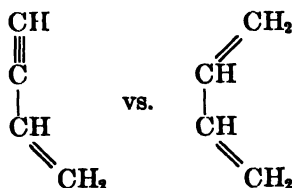
V. POLYENES

Since the conjugated polyenes possess the structure C=C—C=C, it is possible for them to add dienophiles. Further, in a triene such as hexatriene, it is of great importance to determine if the addition of a dienophile takes place at the 1,4- or 1,6-positions, or both; or in higher polyenes, to determine if addition takes place in the 1,4-, 1,6-, 1,8-, or even 1,10-positions. Indications are that, irrespective of the length of the conjugated system, addition invariably takes place at the 1,4-positions, and that each pair of conjugated double bonds in the system acts as an independent unit. Thus 1,3,5,7-octatetraene would add two mole proportions of maleic anhydride to form 1,2,3,4,1',2',3',4'-octahydro-2,3,2',3'-tetracarboxydiphenyl dianhydride:
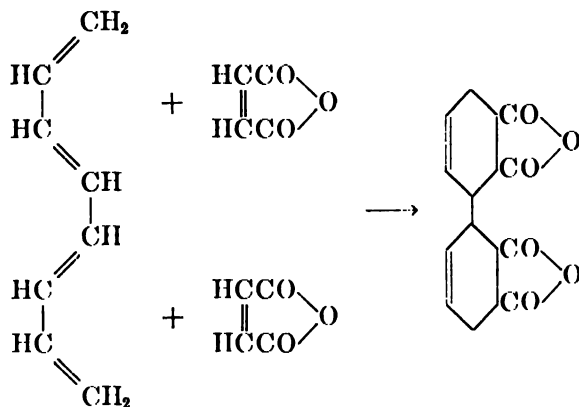
A. Trienes, tetrenes, etc.

The simplest conjugated triene, 1,3,5-hexatriene, has been studied more thoroughly than any other polyene. It was first studied by Farmer and Warren (199), who obtained adducts with both *cis*- and *trans*-hexatrienes. They assigned structure I to the adduct obtained with maleic anhydride, the formation of which involves a rearrangement of the unattacked terminal double bond as well as the usual double-bond shift of a 1,4-addition to a conjugated
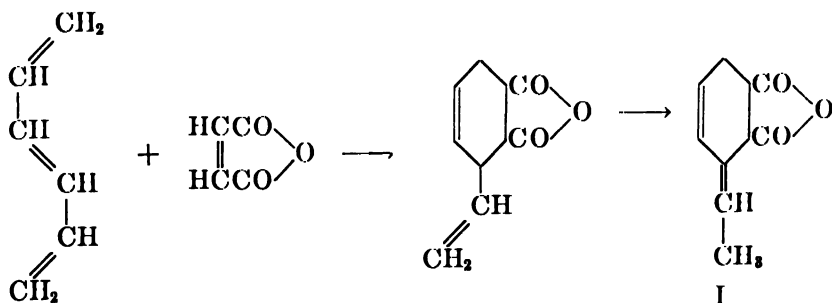
diene. Kharasch, Nudenberg, and Sternfeld (267) claim that the structure is not that given by Farmer and Warren, but is that of 3-vinyl-1,2,3,6-tetra-

hydrophthalic anhydride, evidence being adduced from spectroscopic data. If conditions of the addition are drastic enough to cause the double-bond shift postulated by Farmer and Warren, it would seem that they would be sufficiently drastic to cause further wandering into the ring, since in the terpenes semicyclic double bonds such as this exhibit a marked tendency to wander into the ring, particularly under the influence of acids. The resulting product is usually a conjugated cyclic diene, which adds dienophiles with great avidity. Since hexatriene adds but 1 mole of maleic anhydride, support is given the Kharasch structure. Although the Farmer and Warren adduct structure is that of a conjugated diene, it would not be expected to add maleic anhydride without a preliminary double-bond rearrangement, because of the fixed *trans*-butadienoid structure of this compound.

Much of the confusion may be cleared up by the discovery that the 1,3,5-hexatriene of Farmer and Warren contained cyclohexadiene (397).

Kharasch and Sternfeld (268) prepared 1,3,5-hexatriene by the reaction of allyl chloride with a solution of sodium amide in liquid ammonia. In this preparation a diene reaction was noted between hexatriene and allyl chloride:

$$\text{(structure)} \quad + \quad \begin{array}{c} CH_2 \\ \| \\ CHCH_2Cl \end{array} \quad \longrightarrow \quad \text{(structure)}CH_2Cl$$
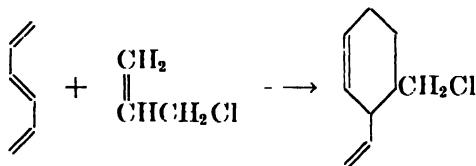
The product could have been the meta-isomer, but this was proved not to be the case. This reaction is quite unusual, for it occurs at $-33°C$. with a dienophile which does not possess the activating carbonyl group.

Butz and his coworkers have studied additions of other dienophiles to 1,3,5-hexatriene. α-Naphthoquinone (99) gave 1,1a,4,4a-tetrahydro-1-vinyl-9,10-anthraquinone, in agreement with Kharasch's postulates concerning the structure of the side chain of hexatriene adducts. 4-Hydroxytoluquinone acetate and 1-aldehydocyclopentene give compounds which are thought to be II and III, respectively:

$$\text{II} \qquad\qquad\qquad \text{III}$$
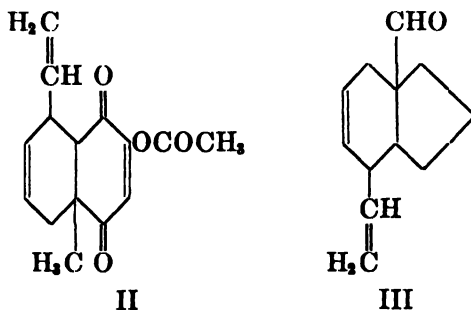
In the case of II, the obvious alternative is an adduct containing an angular acetoxyl group. Presumably the facility of formation of angular groups is inversely proportional to their size. Since the methyl group is smaller than

the acetoxyl group, the angular methyl group should be formed preferentially; actually, both are formed.

The adduct with α-naphthoquinone may be oxidized by air to α-vinyl-9,10-anthraquinone. Butz (98, 99) opines that the structures given for the adducts with 4-hydroxytoluquinone acetate and with 1-formylcyclopentene are the "most probable" structures (II and III), but says that the structure assigned to III is tentative. It is certain, however, that angular groups exist in the compounds represented by II and III.

Robinson, Walker, and Todd (310) assert that 1,3,5-hexatriene does not add 1-methyl-1-cyclohexen-3-one.

Kharasch and his students (267) have extended their hexatriene synthesis to the preparation of 2,5-dimethyl-1,3,5-hexatriene, using methallyl chloride (3-chloro-2-methyl-1-propene). This adds maleic anhydride, giving the expected compound, 1,2,3,6-tetrahydro-4-methyl-6-isopropenylphthalic anhydride.

Vitamin A and related compounds, such as bixin, the carotenes, lycopene, and the xanthenes, should be capable of adding one or more moles of maleic anhydride by virtue of their long-chain conjugated systems. Kuhn and Wagner-Jauregg (273) have demonstrated addition of maleic anhydride to dyes of the bixin and carotene series. Vitamin D_2 (calciferol) is a highly substituted ring-fused hexatriene which adds maleic anhydride (368). It reacts much less readily, however, than does vitamin A (124). A separation of the vitamin D of fish-liver oils from the accompanying vitamin A and carotene (124) is based upon this fact.

Arbuzov (54, 57) has added α-naphthoquinone to alloöcimene. Though the structure of the product was not proved, evidence was secured which indicated that the structure was IV rather than V. Alloöcimene also adds croton-aldehyde and acrolein, but Arbuzov (58) neither proved the structure nor made an assumption or suggestion as to which of the four possible structures for each adduct was the correct one. The adducts appeared to be chemical individuals rather than mixtures.

Alloöcimene adds maleic anhydride (192, 238, 407) to give a product presumed to be VI, although the alternative structure (VII) has not been disproved.

IV   V

VI   VII
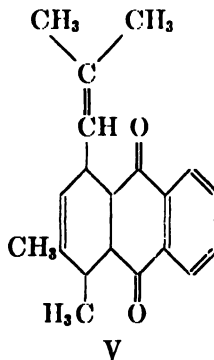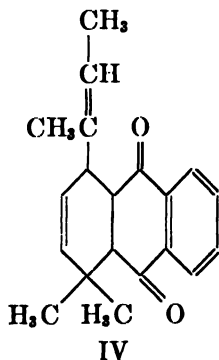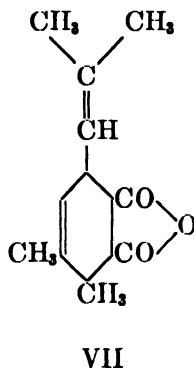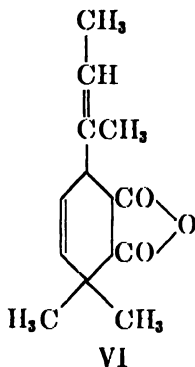
Diphenylpolyenes were investigated by Diels, Alder, and Pries; also by Kuhn and Wagner-Jauregg (152, 273). 1,6-Diphenyl-1,3,5-hexatriene adds maleic anhydride in the 1- and 4-positions. 1,8-Diphenyloctatetraene adds 1 mole of maleic anhydride in boiling xylene at the 1- and 4-positions; by fusing the generators together, 2 moles of maleic anhydride were added. In boiling xylene 2 moles of maleic anhydride are added to give an isomer which yields p-tetraphenyl on decarboxylation and oxidation, thus showing that the second mole of maleic anhydride adds at the 5- and 8-positions. The tetraene also added 2 moles of fumaroyl chloride.

1,10-Diphenyl-1,3,5,7,9-decapentaene adds 2 moles of maleic anhydride. Decarboxylation and oxidation of the two isomeric products formed gave a material which appeared to be 1,2-bis-p-xenylethylene, indicating that the 2 moles of maleic anhydride had added at the 1-, 4-, 7-, and 10-positions. 1,12-Diphenyl-1,3,5,7,9,11-dodecahexaene appeared to add 3 moles of maleic anhydride; oxidation and decarboxylation of the product gave a material which appeared to be p-quinquephenyl. The important conclusions of the investigators were (a) that the diphenylpolyenes add maleic anhydride in positions which correspond with those in butadiene and (b) that the positions nearest the phenyl groups are the most reactive. This latter conclusion arose from the fact that degradation of the adducts from 1,10-diphenyldecapentaene appeared to give 1,2-bis-p-xenylethylene rather than ω-(p-xenyl)styrene.

B. Dienynes

Several dienynes were discussed on pages 380–382 as examples of enynes, for that particular field has not been well developed as yet. Rapid progress is being made, however. Two other dienynes have been studied,—namely, 6,9-dimethyltetradeca-5,9-dien-7-yne (92), and 4,7-di-n-propyldeca-3,7-dien-5-yne (100). These react with 2 moles of maleic anhydride, but the products appear to be amorphous and not well established. Referring to page 382, the ring structure of the adduct of 2,5-dimethylhexa-1,5-dien-3-yne and maleic anhydride (100) was proved by degradation to 1,5-dimethylnaphthalene.

VI. HOMOCYCLIC DIENES

A. General

Under this heading are discussed dienes which contain their dienic double bonds in a ring composed exclusively of carbon atoms, such as cyclopentadiene and cyclopentadienone; also, compounds in which one dienic double bond is situated in a ring and the other is situated either in a side chain or else in a second ring which usually is not fused to the first ring. All rings are aliphatic in character; compounds in which one or both of the dienic double bonds are situated in a completely aromatic ring are reserved for later discussion.

1,3,5-Cyclohexatriene (benzene) has never been observed to add dienophiles, although a number of cases are known in which one of the dienic double bonds is located in a lone benzene ring and one case (9,10-anthraquinone) appears to be known in which both dienic double bonds are located in a lone benzene ring.

The first recorded addition of a dienophile to cyclopentadiene (aside from its polymerization reaction, studied by Staudinger (337) and by Bergel and Widmann (81)) was made by Albrecht (379) in 1906, using certain quinones and unsaturated ketonic compounds. Diels and Alder (136) clarified the structure of the adducts, and other illustrations of the diene synthesis with cyclic dienes were published shortly thereafter.

The general statement postulated for the diene synthesis (page 320) holds true for the homocyclic dienes, and may be written in the forms
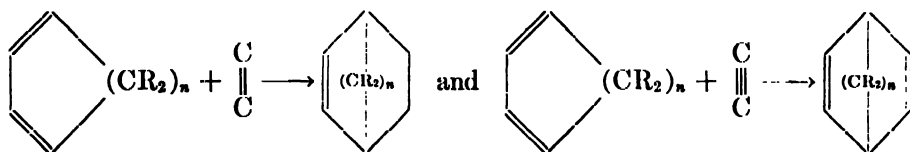
where R may be hydrogen, oxygen, or nearly any alkyl or aryl radical. Theoretically, n may be any number, but the highest value studied appears to be 3.

The adducts obtained from these cyclic dienes have a most interesting behavior on distillation at atmospheric pressure. Adducts of cyclopentadiene and its homologs either distil unchanged or else decompose into their generators. Adducts of cyclopentadienones usually evolve carbon monoxide, and the resulting product is either a benzene derivative (if derived from an acetylenic dienophile) or else a substituted cyclohexadiene which is easily oxidized to such a derivative. Occasionally the cyclohexadiene dehydrogenates spontaneously on heating (Allen). Adducts of 1,3-cycloheptadienes either distil unchanged or else decompose into their generators. The adducts of 1,3-cyclohexadienes with acetylenic dienophiles decompose on distillation to give an olefin and a benzene derivative. Fusion of adducts of cyclohexadienes and quinones in the presence of air leads to simultaneous oxidation and splitting of olefin. If a temperature is employed which is below that required to split out olefin, then oxidation occurs to give a compound which splits out olefin at the

higher temperature. The products of olefin-splitting are aromatic quinones. Dismutation of partially hydrogenated quinone adducts may be brought about by acetic anhydride in certain instances. When adducts of cyclohexadienes with olefinic dienophiles are distilled, more or less deep-seated changes occur. The usual reaction is to give a benzene derivative and the reduced dienophile. In this manner, the adducts of α-phellandrene and of 1,3-menthadiene (α-terpinene) with maleic anhydride give succinic anhydride and p-cymene.

Below is a summary of the reactions indicated in the preceding paragraph:

(8)
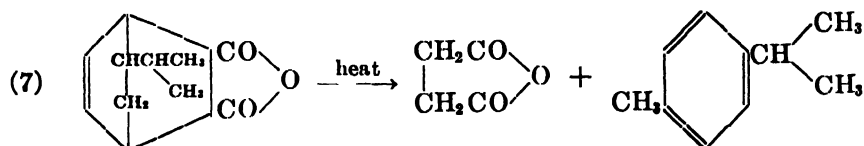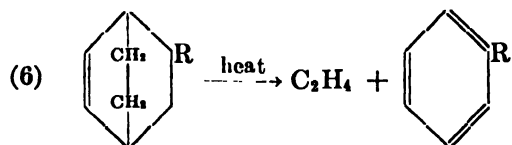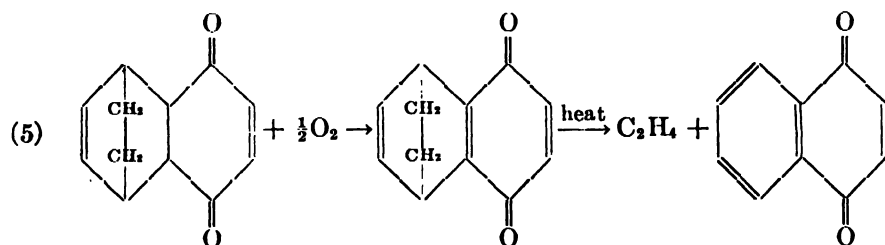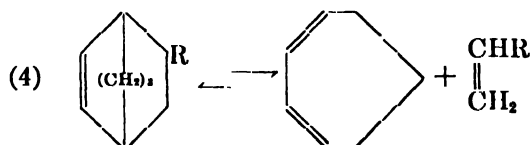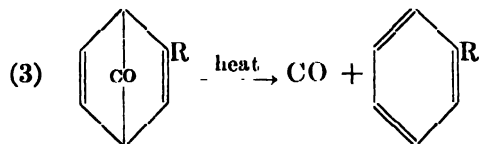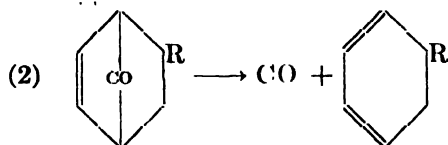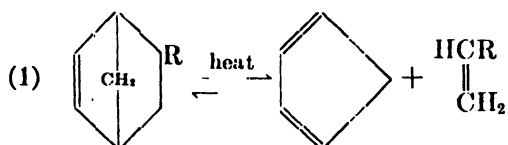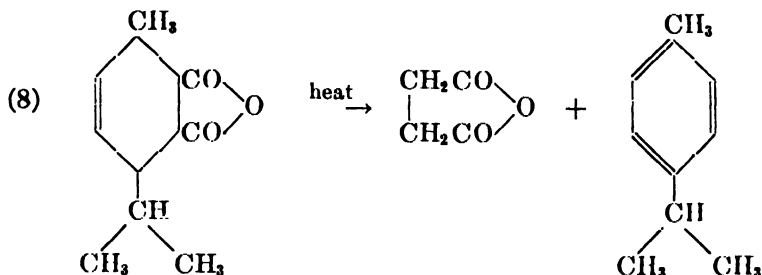
Specific examples of the foregoing reaction types are the decomposition of the cyclohexadiene–acetylenedicarboxylic ester adduct to give ethylene and diethyl phthalate (18); the fusion of the adduct from 2 moles of cyclohexadiene and 1 mole of p-benzoquinone to give ethylene and 9,10-anthraquinone (34), atmospheric oxidation occurring simultaneously; the decomposition of the adduct of α-phellandrene and acetylenedicarboxylic ester to give isopropylethylene and 4-methylphthalic ester (147); and the dismutation by acetic anhydride of a partially hydrogenated adduct of cyclopentadiene with α-naphthoquinone to give α-naphthohydroquinone diacetate, cyclopentadiene, and water (which appears as acetic acid) (153).

The ethylene and carbonyl bridges are not the sole types which split out on heating, however. Lactone bridges (—CO—O—) will split out carbon dioxide on heating; this bridge is not particularly heat-stable. A good example of this reaction is found in the addition of maleic anhydride to cumalin and its derivatives, discussed elsewhere in this review. Another type is the splitting of ethylene from the partially hydrogenated adducts of certain furan derivatives with acetylenedicarboxylic ester to give dicarboxylated furan esters.

B. Cyclopentadienes

The most extensively studied of the homocyclic dienes is cyclopentadiene itself. It has been found to react with a wide variety of dienophiles, giving the anticipated products. Most of these reactions are listed in table 4; others may be found in tables 1 and 2. Polymerization reactions of the compound are discussed in a subsequent section devoted to dimerization (see page 430).

An interesting reaction of the adduct with azodicarboxylic ester is the splitting of the endomethylene bridge by hydrogen chloride to give the adduct of 1-methyl-4-chlorobutadiene and azodicarboxylic ester:
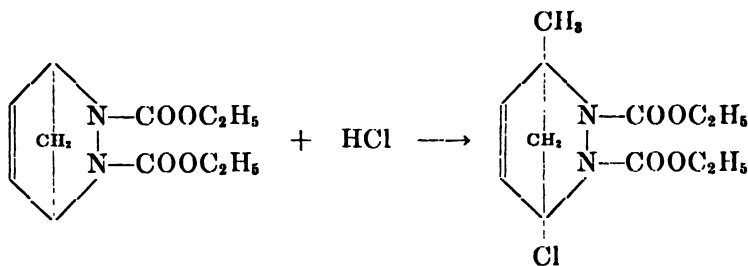
TABLE 4

Additions of dienophiles to cyclopentadiene
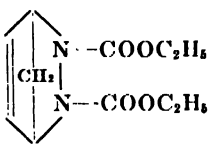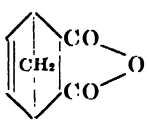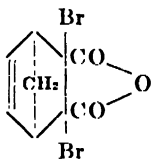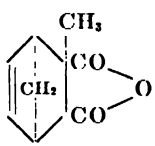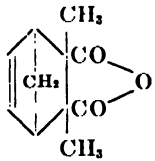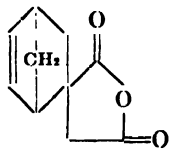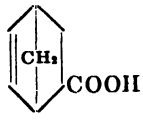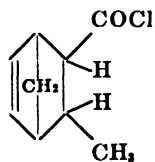
DIENOPHILE	ADDUCT	REFERENCE
Ethylene	3,6-Endomethylenecyclohexene	(411)
Azodicarboxylic ester	CH₂ ⟨ring⟩ N—COOC₂H₅ / N—COOC₂H₅	(157)
Maleic anhydride	CH₂ ⟨ring⟩ CO—O—CO	(136, 137, 166)
Dibromomaleic anhydride	Br / CH₂ ⟨ring⟩ CO—O—CO / Br	(151)
Citraconic anhydride	CH₃ / CH₂ ⟨ring⟩ CO—O—CO	(136)
Pyrocinchonic anhydride	CH₃ / CH₂ ⟨ring⟩ CO—O—CO / CH₃	(146, 166)
Itaconic anhydride	CH₂ ⟨ring⟩ O / O—O	(136)
Acrylic acid	CH₂ ⟨ring⟩ COOH	(35, 37, 136)
trans-Crotonoyl chloride	COCl / H / CH₂ ⟨ring⟩ H / CH₃	(35)

TABLE 4—*Continued*
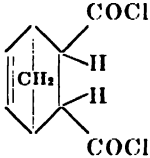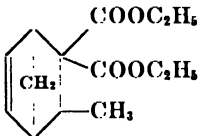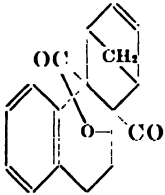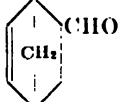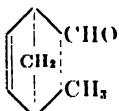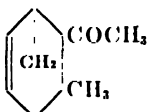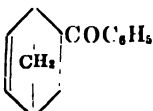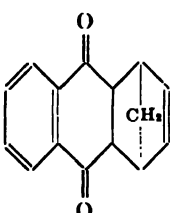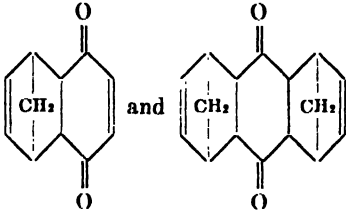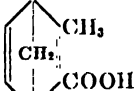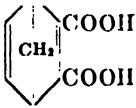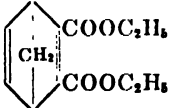
DIENOPHILE	ADDUCT	REFERENCE
Fumaroyl chloride...........		(35)
Ethylidenemalonic ester......		(18)
1,2-Dihydro-3,4-naphthalic anhydride..		(213)
Acrolein		(35, 136, 144, 150, 263)
Crotonaldehyde..............		(114, 150)
Ethylideneacetone		(139)
Benzoylethylene..............		(47)
α-Naphthoquinone...........		(153)

TABLE 4—*Concluded*

DIENOPHILE	ADDUCT	REFERENCE
p-Benzoquinone.............	(structure) and (structure)	(23, 153, 196)
cis- and *trans*-1,2-dibenzoyl-ethylenes.....	(structure) COC_6H_5 COC_6H_5	(3, 6)
Propiolic acid	(structure) $COOH$	(39)
Tetrolic acid................	(structure) CH_3 $COOH$	(166)
Acetylenedicarboxylic acid ...	(structure) $COOH$ $COOH$	(147)
Acetylenedicarboxylic ester ..	(structure) $COOC_2H_5$ $COOC_2H_5$	(147)

Certain homologs and derivatives of cyclopentadiene have been investigated. Damsky (128) prepared a trimethylcyclopentadiene by distillation of the calcium salt of either α- or β-camphylic acid. Wandering of a methyl group or of a double bond (43) occurs during the pyrolysis, and the product is not 1,1,2-trimethyl-2,4-cyclopentadiene; however, it does contain a conjugated system, inasmuch as it adds vinyl acetate (44) at elevated temperatures and adds maleic anhydride and acetylenedicarboxylic ester more easily (45). If the decarboxylations of the α- and β-camphylic acids are conducted in quinoline with a copper chromate catalyst, the reactions take place at a temperature which is too low to result in isomerization of the product, and 1,1,2-trimethyl-2,4-cyclopentadiene is obtained (45). This diene is useful for the synthesis of terpinoid derivatives of bornane.

At elevated temperatures, vinyl acetate adds to 1,1,2-trimethylcyclopenta-diene to give a mixture of *dl*-dehydrobornyl acetate and *dl*-dehydroepibornyl acetate. Hydrogenation, hydrolysis, and oxidation of the former adduct give *dl*-camphor. The diene also adds maleic anhydride, acetylenedicarboxylic acid, and acetylenedicarboxylic dimethyl ester to give the adducts I, II, and III:

The camphylic acid esters add maleic anhydride, vinyl acetate, acetylenedi-carboxylic acid, and acetylenedicarboxylic esters to give adducts of anticipated structures (44, 45). The maleic anhydride adducts of methyl α- and β-camphylates are VI and VII, respectively.
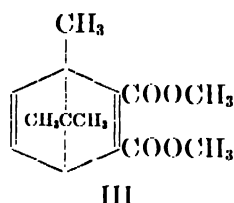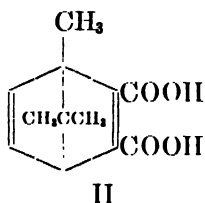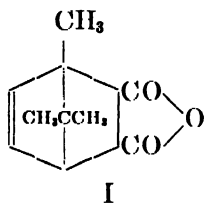
Adduct III may be partially reduced by platinum and hydrogen to give IV, oxidation of which by nitric acid gives a trimethylcyclopentanedicarboxylic acid (V).
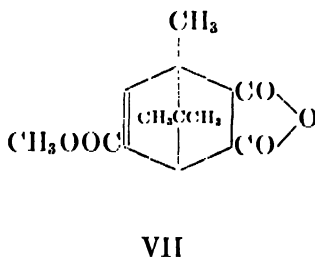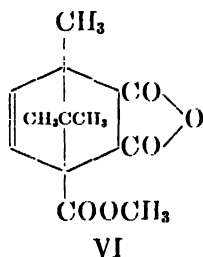
Owing to the fact that two structures are theoretically possible through the use of vinyl acetate as a dienophile, the structures of the vinyl acetate addition products are not certain.

Potassium powder, suspended in benzene or other suitable medium, reacts with cyclopentadiene to give potassium cyclopentadiene, presumably VIII.

This reacts with benzyl chloride to give a mixture of the 2- and 3-benzylcyclo-pentadienes, which react with maleic anhydride to give the expected adducts (12, 13). Oxidation of the adduct derived from the 3-benzyl isomer (IX)

VIII   IX
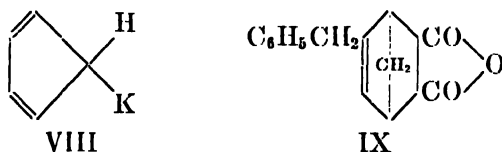
gives benzoic acid and *cis-,cis-,cis-,cis*-1,2,3,4-cyclopentanetetracarboxylic acid (21).

C. *Cyclopentadienones*

Of particular interest are the reactions of the phenyl- and chloro-substituted cyclopentadienones, for these combine the structures of reactive diene and reactive dienophile. The simpler members of the series are so reactive that they have not been isolated in the monomeric state, although their transitory existence may be demonstrated. The higher members of the series are still highly reactive, adding such inert dienophiles as acetylene, butadiene, benzonitrile, and acenaphthylene. Those cyclopentadienones with phenyl groups substituted on the 1- and 4-positions of the butadienoid system of cyclopentadienone do not dimerize, probably because of the stereochemical difficulties involved. These compounds are a fine example of the fact that the carbonyl group will enhance the reactivity of a diene as well as that of a dienophile.

The first of these cyclopentadienones to be investigated was tetrachlorocyclo-pentadienone, by T. Zincke and his collaborators in the period 1893–1912 (376, 377, 378). It was first observed that hexachlorocyclopenten-3-one was reducible to 1,2,4,5,5-pentachlorocyclopenten-3-one by stannous chloride during the course of 1 hr. When boiled with water, this substance lost hydrogen chloride to form tetrachlorocyclopentadienone; this compound dimerized immediately to a compound which lost the elements of phosgene (apparently the phosgene was hydrolyzed by water to carbon dioxide and hydrogen chloride) and formed hexachloroindone. It was found later that prolonged reduction (one to two days) of hexachlorocyclopenten-3-one by stannous chloride at room temperature gave the dimer of tetrachlorocyclopentadienone. The stannous chloride probably served no useful function after the initial reduction; mere standing in water was no doubt sufficient for the tetrachlorocyclopenta-dienone to form and dimerize. Boiling the dimer with water gave hexachloro-indone, carbon dioxide, and hydrogen chloride.

In 1912 it was found that phosgene was not liberated as such. It was shown that the dimer of tetrachlorocyclopentadienone loses carbon monoxide at its melting point to form an octachlorodihydroindone, and that further heating causes double-bond rearrangement to octachlorohydrindone. This is easily

reduced by stannous chloride to give hexachloroindone. Hence the formation of hexachloroindone by boiling the dimer of tetrachlorocyclopentadienone with water is due, in part at least, to reduction of octachlorohydrindone by carbon monoxide or one of its immediate precursors. The various reactions are shown below diagrammatically:
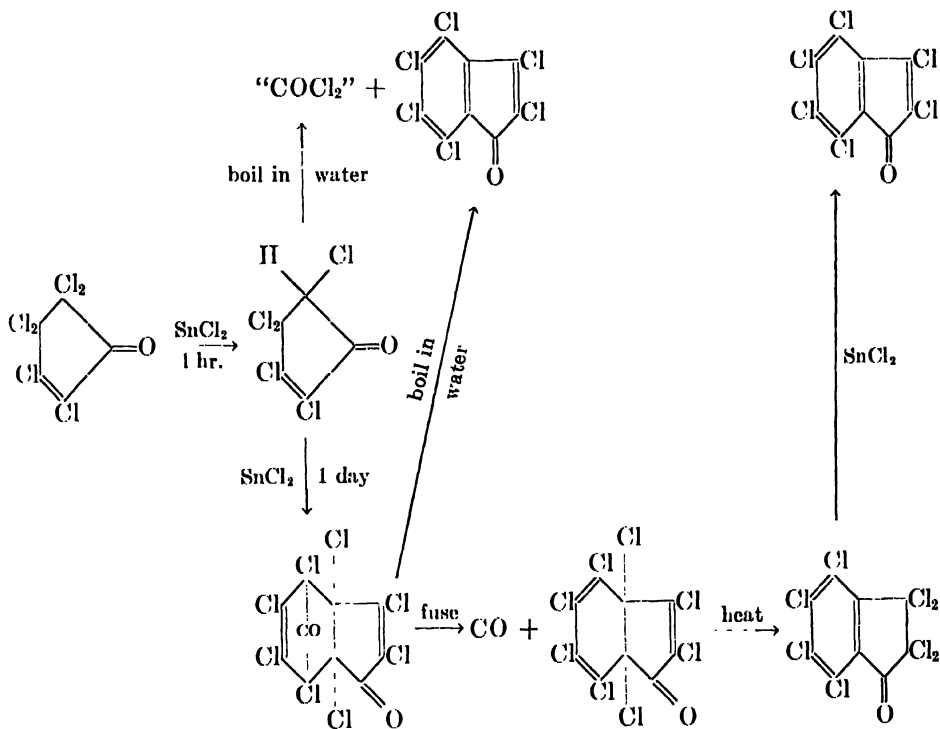
The phenylated 2,4-cyclopentadienones which have been studied include 3,4-diphenyl-, 2,3,4-triphenyl-, 2,3,5-triphenyl-, and 2,3,4,5-tetraphenyl-cyclo-pentadienones. The last named is also known as tetracyclone. Allied to these purely phenyl-substituted cyclopentadienones are 2,5-diphenyl-3,4-(o,o'-bi-phenylene)cyclopentadienone (phencyclone), and 2,5-diphenyl-3,4-(peri-naph-thylene)cyclopentadienone (acecyclone). None of the 2,5-diphenylated compounds dimerizes even under extreme conditions of temperature. It is possible, therefore, to obtain all but the first two cyclopentadienones listed above in the monomeric state. These monomers are all highly colored substances.

3,4-Diphenylcyclopentadienone is formed from anhydracetonebenzil in several ways (50, 51), one being by dehydration with acid. It enjoys only a transitory existence, however, dimerizing almost immediately under the conditions employed:
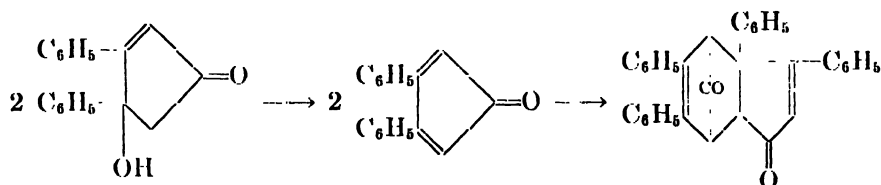
By using a large excess of maleic anhydride as the dehydrating agent, the existence of the monomeric form of 3,4-diphenylcyclopentadienone may be shown (52) by the formation of considerable quantities of an adduct derived from maleic anhydride and the monomer:
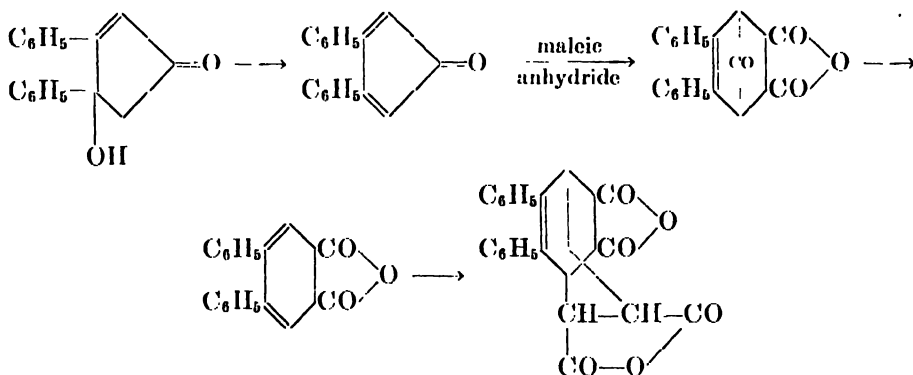
In similar fashion (178), the heating of a mixture of anhydracetonebenzil with diphenylacetylene will yield a small amount of 1,2,4,5-tetraphenylbenzene, together with much 3,4-diphenylcyclopentadienone dimer and its pyrolysis products. The same product, 1,2,4,5-tetraphenylbenzene, may be obtained in quantitative yield by the reaction of 2,3,5-triphenylcyclopentadienone (178) with phenylacetylene. The other product which is theoretically possible (1,2,3,5-tetraphenylbenzene) is not produced:
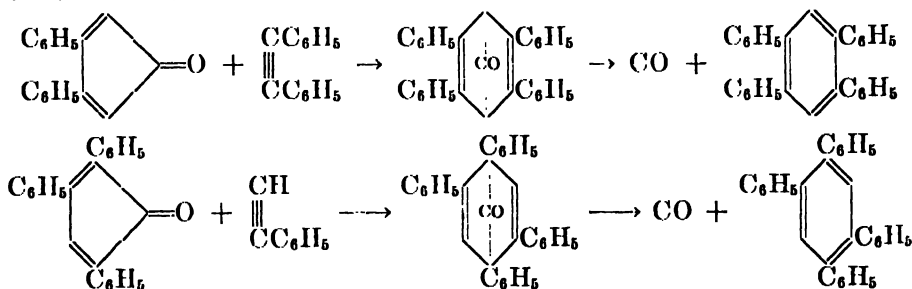
2,3,4-Triphenylcyclopentadienone is not known in the monomeric state, and dimerizes almost on formation. As in the case of 3,4-diphenylcyclopentadienone, its transitory existence may be shown by heating triphenylcyclopentenolone with phenylacetylene, phenylpropiolic acid, or diphenylacetylene. The products formed with these three dienophiles are 1,2,3,4-tetraphenylbenzene, 2,3,4,5-tetraphenylbenzoic acid, and pentaphenylbenzene, respectively (178):

The chemical reaction schemes at the top of the page show three Diels-Alder syntheses:

$$C_6H_5 \text{ (diene structure)} = O + \begin{array}{c} CC_6H_5 \\ \parallel \\ CH \end{array} \rightarrow \text{(bridged structure, CO)} \rightarrow CO + \text{(benzene ring product)}$$

$$C_6H_5 \text{ (diene structure)} = O + \begin{array}{c} CC_6H_5 \\ \parallel \\ CC_6H_5 \end{array} \rightarrow \text{(bridged structure, CO)} \rightarrow CO + \text{(benzene ring product)}$$

$$C_6H_5 \text{ (diene structure)} = O + \begin{array}{c} CC_6H_5 \\ \parallel \\ CCOOH \end{array} \rightarrow \text{(bridged structure, CO)} \rightarrow CO + \text{(benzene ring product, COOH)}$$

It will be noted that loss of the endocarbonyl bridge occurs in each of the above syntheses. With acetylenic dienophiles this is especially true, the resulting carbonyl bridge being highly unstable toward heat. This is true to a lesser degree with the endoethylene and endolactone bridges. In the above cases, the instability of the carbonyl bridge is so great that these intermediates usually cannot be isolated. When the dienophile is an acid, the endocarbonyl compound can sometimes be obtained. Room-temperature dimerization of those cyclopentadienones which are capable of dimerization likewise gives endocarbonyl compounds. In this fashion the dimer of 3,4-diphenylcyclopentadienone loses carbon monoxide at about 230°C. to give 1,5,6,9-tetraphenyl-9,10-dihydroindone (52) and carbon monoxide. If maleic anhydride is present, an adduct is formed with this cyclohexadiene derivative:

The reaction scheme shows a structure with C_6H_5 groups and CO bridge converting to $CO +$ a product with maleic anhydride, leading to a final tricyclic structure with C_6H_5 groups and HCCO/HCCO anhydride bridge.
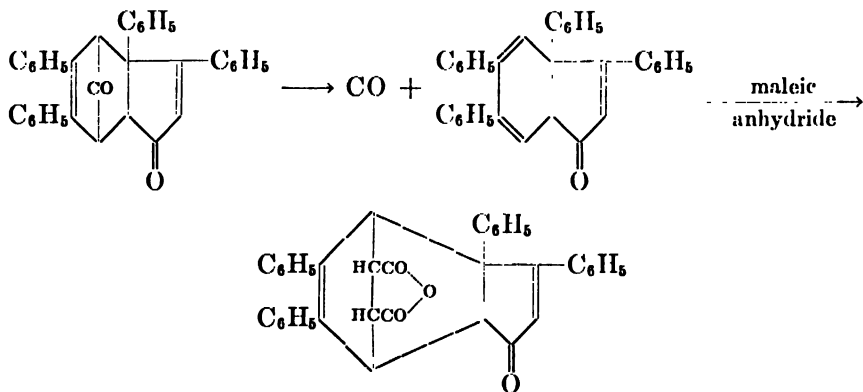
In the absence of maleic anhydride, continued heating of 1,5,6,9-tetraphenyl-9,10-dihydroindone at 250°C. results in rearrangement to 1,2,5,6-tetraphenyl-hydrindone. Care is required, therefore, for success in isolating the isomeric 9,10-dihydro compound, for heating at 230°C. for any considerable length of time will also result in extensive rearrangement (52):
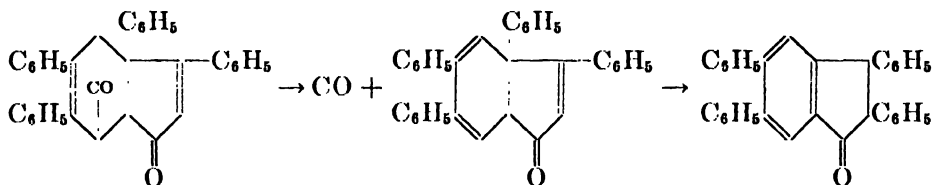
This rearrangement is analogous to that observed by Zincke (*vide supra*). The structure of the final product was confirmed by degradation to *o*-terphenyl. By heating the 9,10-dihydro compound with sulfur, 1,5,6-triphenylindene and thiophenol were formed (52). This is one of the few cases on record in which an angular aryl group is removed by sulfur dehydrogenation.

Tetracyclone (2,3,4,5-tetraphenylcyclopentadienone) was first prepared by Ziegler and Schnell (374) and almost simultaneously by Loewenbein and Ulich (287). It is a highly colored compound (red), as are all the monomeric arylated cyclopentadienones. Dilthey (180) prepared the compound by reaction of benzil with dibenzylketone to give a diphenylanhydracetonebenzil which could be dehydrated easily to tetracyclone. By substituting phenanthrenequinone or acenaphthalenequinone for benzil, one obtains phencyclone or acecyclone (180).

Tetracyclone is a very reactive dienic compound, though it does not dimerize. It not only adds comparatively unreactive dienophiles with ease, but it reacts with unsaturated substances which are not ordinarily thought of as dienophiles. Accordingly, it reacts with benzonitrile, liberating carbon monoxide and forming pentaphenylpyridine (181). A reaction is also shown with sulfur, the reaction products being carbon monoxide and thionessal (tetraphenylthiophene); a similar reaction is shown by 2-(*p*-anisyl)-3,4,5-triphenylcyclopentadienone, which gives carbon monoxide and the corresponding *p*-methoxythionessal (181; see also J. prakt. Chem. [2] **151**, 185 (1938)).

Maleic anhydride adds to tetracyclone, and here the various intermediates may be isolated. The first product is 3,6-endocarbonyl-1,2,3,6-tetrahydro-3,4,5,6-tetraphenylphthalic anhydride; at higher temperatures this loses carbon monoxide to form 3,4,5,6-tetraphenyl-1,2-dihydrophthalic acid. At still higher temperatures, hydrogen is evolved and 3,4,5,6-tetraphenylphthalic acid is formed (49, 51, 182, 184):
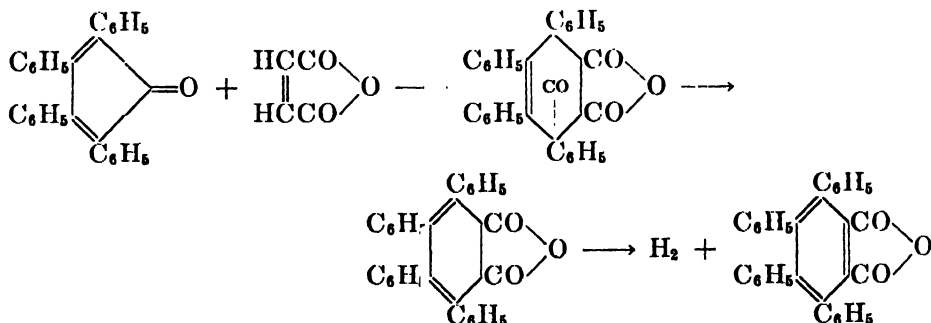
The conversion of the dihydro acid to tetraphenylphthalic acid is best accomplished by use of a dehydrogenating agent, such as sulfur, or by using an oxidizing

solvent (nitrobenzene) for the reaction mixture. If the formation of tetraphthalic acid is carried out in one step from tetracyclone and maleic anhydride, the final product contains small amounts of the adduct of maleic anhydride with the dihydrophthalic acid:
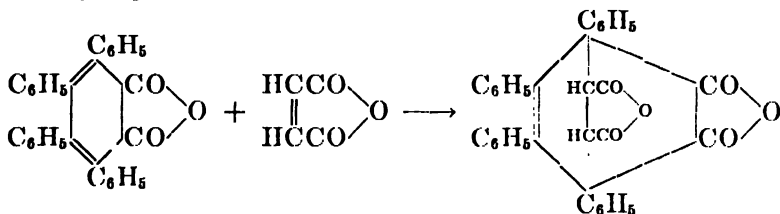
A considerable number of other dienophiles has been added to tetracyclone. Indeed, this compound has been the most thoroughly studied of the cyclopentadienones with regard to activity in the diene synthesis. Benzalacetophenone was reported (49) not to add to tetracyclone, but it was shown later that addition would occur under forcing conditions (47), the products being carbon monoxide and 2,3,4,5,6-pentaphenylbenzophenone. Acetylene is added, even at 100°C., to give carbon monoxide and 1,2,3,4-tetraphenylbenzene (182). Phenylacetylene gives carbon monoxide and pentaphenylbenzene (182), and stilbene gives hydrogen, carbon monoxide, and hexaphenylbenzene of melting point 426°C. (182). The same product was obtained without evolution of hydrogen by the use of diphenylacetylene in place of stilbene (178, 181, 182). The melting point of the hexaphenylbenzene thus obtained was nearly 200°C. higher than that reported previously in the literature, which corresponded more closely with that of 1,2,4,5-tetraphenylbenzene. The previous preparation was made by the interaction of phenylmagnesium bromide with hexachlorobenzene; duplication of this work gave a similar compound (177). Molecular-weight determinations showed that the previously reported hexaphenylbenzene was in reality a tetraphenylbenzene, while the compound produced by the addition of diphenylacetylene or stilbene to tetracyclone had an observed molecular weight agreeing with the theoretical value for hexaphenylbenzene. It has an uncorrected melting point of 426°C. The previous report of the synthesis of hexaphenylbenzene must be regarded as an error.

Diphenylbutadiyne (181) also adds to tetracyclone with evolution of carbon monoxide and the product is (pentaphenylphenyl)phenylacetylene. Further reaction, which would produce decaphenylbiphenyl, does not appear to occur. With butadiene (181), such double addition does occur; carbon monoxide is evolved and the product is a mixture of octaphenylbiphenyl with various hydrogenated octaphenylbiphenyls. Cyclohexene adds in a forced reaction (181), giving carbon monoxide, hydrogen, and Bz-tetraphenyltetralin. Phenylbromoacetylene (181) adds easily to give pentaphenylbromobenzene. Acenaphthylene (176) gives 2,3,4,5-tetraphenyl-1,6-(peri-naphthylene)benzene. Benzoylethylene (47) adds, with evolution of carbon monoxide and hydrogen, to give 2,3,4,5-tetraphenylbenzophenone. Phenylpropiolic aldehyde (182) gives carbon monoxide and pentaphenylbenzaldehyde, and phenylpropiolic nitrile gives carbon monoxide and pentaphenylbenzonitrile.

The additions of unsaturated dibasic acids and certain of their esters to tetracyclone often result in products which contain the carbonyl bridge. The bridge can be removed by further heating and finally an aromatic acid or ester may be formed. This was shown to be the case in the addition of maleic anhydride to tetracyclone. True adducts containing the carbonyl bridge are rarely isolable in other cases. Of the dienophiles mentioned above, none undergoes reaction at temperatures lower than the temperatures required for complete decomposition of their adducts, save for maleic anhydride. Additions of the methyl and ethyl esters of acetylenedicarboxylic acid require too high a temperature to allow isolation of such intermediates (49, 184), and the products are methyl and ethyl tetraphenylphthalates. The same products are obtainable from the corresponding esters of maleic acid. While no endocarbonyl intermediate can be obtained with dimethyl maleate, such may be obtained with diethyl maleate and with dimethyl fumarate (49), because the temperatures required for reaction with the latter two esters are lower than the decomposition temperatures of the adducts resulting from such addition. Strong heating of these adducts also gives tetraphenylphthalic esters. These esters, being derived from hindered aromatic acids, are difficult to hydrolyze (49), and the ethyl ester of tetraphenylphthalic acid is stable to molten alkali at 360°C. The corresponding acid anhydride, from tetracyclone and maleic anhydride or acetylenedicarboxylic acid, condenses to a fluorenone on treatment with aluminum chloride in boiling benzene (184); more drastic treatment gives a difluorenone.

C_6H_5 C_6H_5 C_6H_5 C_6H_5

CO CO   COOH
  \ /
   O   O

C_6H_5 C_6H_5

O   O
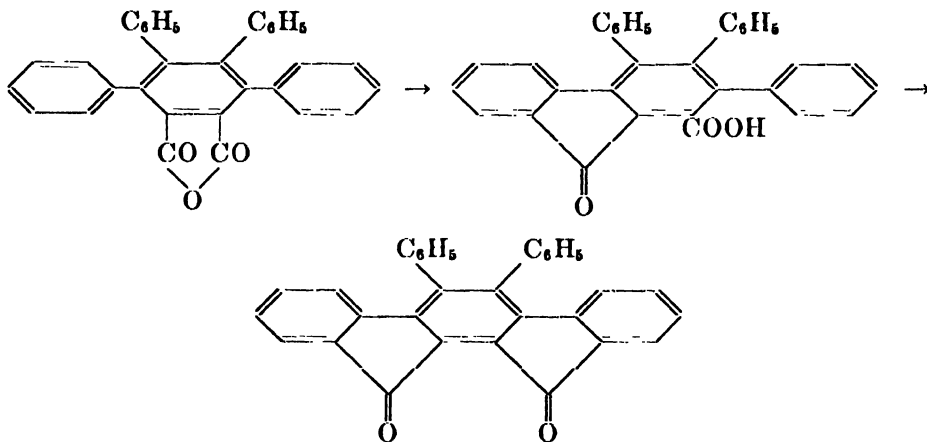
Phenylpropiolic methyl ester (184) requires a high temperature for addition to tetracyclone; consequently the intermediate carbonyl-bridged adduct is not obtainable. The corresponding acid (182, 184) also requires a high temperature for addition; it yields pentaphenylbenzoic acid. This latter acid can be condensed (184) with aluminum chloride to give 1,2,3,4-tetraphenylfluorenone. Tetrolic acid or its ethyl ester (184) gives tetraphenyl-o-toluic acid or its ester.

Diphenylketene does not react (49) with tetracyclone. This supports Staudinger's hypothesis (81) that diphenylketene undergoes 1,2-addition to conjugated and isolated double bonds. Quinones appear not to have been

investigated, at least with tetracyclone, but the fact that adducts containing endocarbonyl bridges may be prepared with phencyclone and quinones lends support to the prediction that such will also be found to be the case with tetracyclone.

Gummitt and coworkers (408) report that tetracyclone adds a mole of cyclopentadiene to give a carbonyl-bridged adduct. In attempting to remove the carbonyl bridge by heating, preferential dissociation took place to give the original generators. No reaction was noted between tetracyclone and furan, pyrrole, N-methylpyrrole, or thiophene.

Allen and van Allan (387) describe 2,5-dimethyl-3,4-diphenylcyclopentadienone as being midway between 3,4-diphenylcyclopentadienone and tetracyclone. This substance is not known in the monomeric form, but in solution its dimer reacts as if it were monomeric. This dissociation of the dimer should be compared with 3,4-diphenylcyclopentadienone, which dimerizes completely and permanently, and with tetracyclone, which does not dimerize at all. Thus, the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone will add acetylene, phenylacetylene, β-nitrostyrene, vinyl phenyl ketone, maleic anhydride, and other dienophiles because of the preliminary dissociation to the monomeric form.

Phencyclone (180) reacts with p-benzoquinone, naphthoquinone, naphthazarin, and naphthazarin diacetate to give adducts containing carbonyl bridges. Heating to elevated temperatures causes loss of carbon monoxide, and dihydroquinones are formed which may be dehydrogenated by atmospheric oxygen or other dehydrogenating agents to give fully aromatic quinones. In order to isolate these intermediates, it is essential that one operate in an inert atmosphere (carbon dioxide). p-Benzoquinone finally gives 1,2,3,4-dibenz-9,10-diphenyl-5,8-anthraquinone; α-naphthoquinone gives 1,2,3,4,6,7-tribenz-9,10-diphenyl-5,8-anthraquinone; and naphthazarin or its diacetate gives 1,4-diphenyl-2,3-(o,o'-biphenylene)-5,8-dihydroxy-9,10-anthraquinone or its diacetate:

(X = hydrogen, hydroxyl, or acetoxyl)
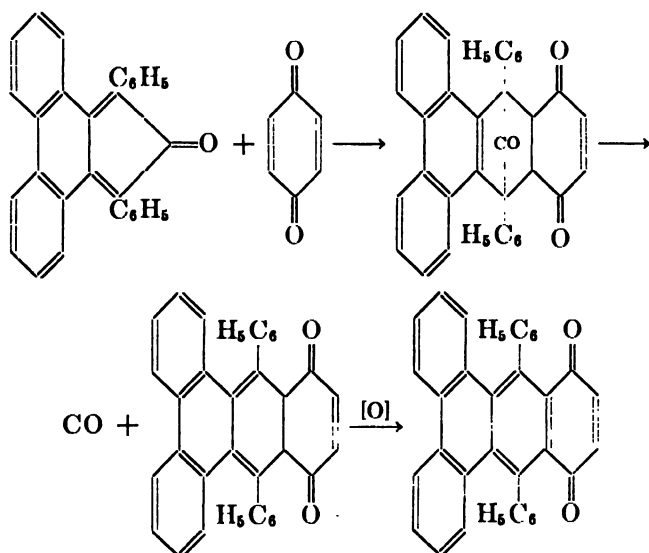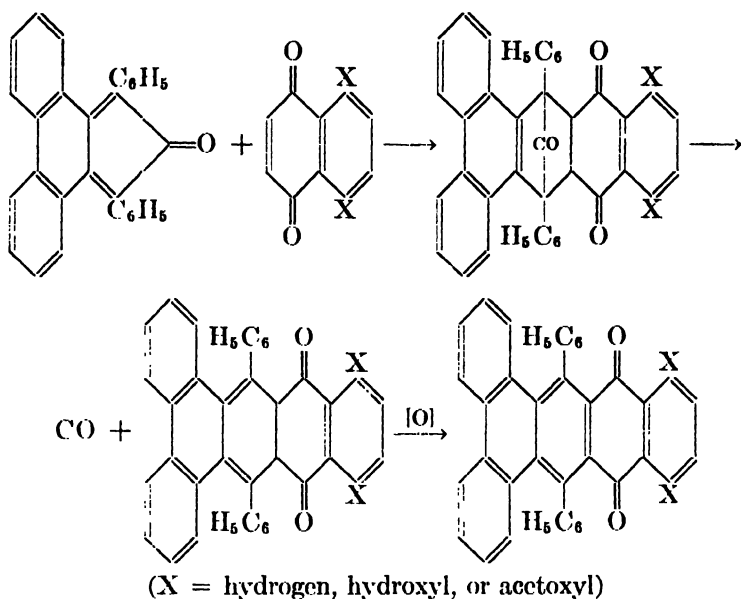
Reduction of these quinones from p-benzoquinone and from α-naphthoquinone would give the corresponding hydrocarbons. It can be seen, therefore, that this method offers means of preparing diphenylated dibenzanthracenes and naphthacenes and related hydrocarbons, some of which may be carcinogenic.

Phencyclone has been added to fumaric acid, maleic acid, and maleic anhydride (183), phenylpropiolic acid (176), phenylacetylene (176), diphenylacetylene (176), and benzoylethylene (47) to give products corresponding with those obtained from tetracyclone. It also reacts with sulfur, but the reaction is more complex than that with tetracyclone; the product is of more or less indefinite composition, for the amount of sulfur utilized ranges between four and five atoms per molecule of phencyclone. When distilled, this sulfurized product affords a 20 per cent yield of biphenylenediphenylthiophene, there being evolved carbon dioxide, carbon monoxide, carbon oxysulfide, and hydrogen sulfide.

Acecyclone shows no reaction whatever with sulfur. It has been shown to add benzoylethylene (47), acetylene (176), and phenylacetylene (176); the structures of the products correspond with those of the tetracyclone series. The adduct with diphenylacetylene (176) is identical with the adduct obtained from tetracyclone and acenaphthylene; acecyclone also adds acenaphthylene to give carbon monoxide and 1,4-diphenyl-2,3,5,6-bis(peri-naphthylene)benzene (176):
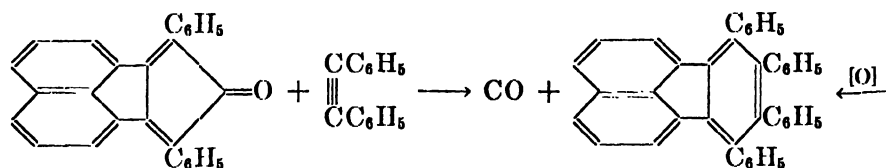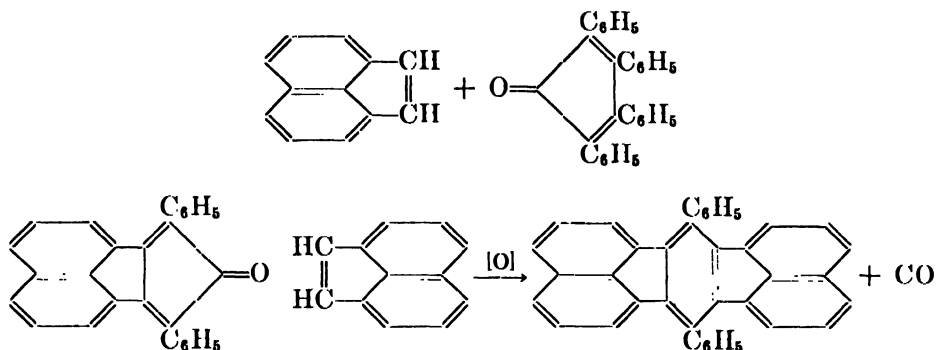
Benzalacetophenone, diphenylketone, and 1,2-dibenzoylethylene could not be added to either phencyclone or acecyclone (49).

D. Fulvenes

Fulvenes are the 1-alkylidenecyclopentadienes, and contain one more double bond than cyclopentadiene. This double bond is conjugated with each of the two double bonds of the cyclopentadiene ring, and at first sight one might think that ambiguity might arise in determining which of the two possible routes (A or B) might be followed by the addition of dienophiles to fulvenes:
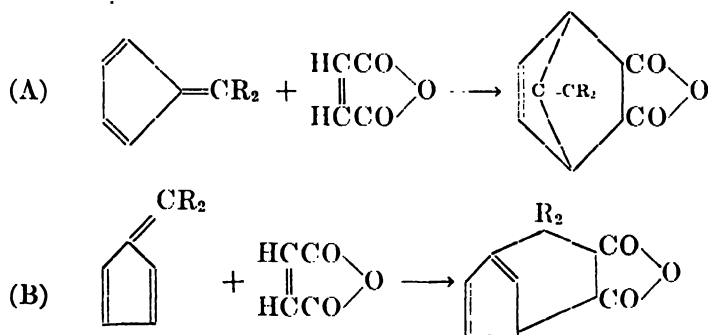
The fact that the postulated addition represented by reaction B would occur through addition to a *trans*-butadienoid system (see page 323) and that addition A would occur through addition to a *cis*-butadienoid system strongly suggests that addition A occurs rather than B. Further, the hypothetical reaction product of B possesses a 1,3-cyclopentadiene ring and therefore should be capable of adding a second mole of dienophile. Only 1 mole of dienophile adds to the fulvenes.

An outstanding characteristic of fulvene adducts is the fact that they are usually dissociated to a greater or less extent when in solution, though stable in the solid state. The extent of dissociation can be estimated colorimetrically in many cases, since the sole colored material in the equilibrium mixture is the fulvene (270). Oftentimes molecular-weight determinations are employed for estimation of the degree of dissociation of these adducts. Equilibrium is at-

tained slowly in these solutions, as may be shown by the gradual increase in color of a solution of a fulvene adduct on standing.

Dimethylfulvene and diphenylfulvene react with maleic anhydride to give adducts which dissociate in solution, as do the maleic anhydride adducts of tetra- and penta-methylenefulvenes (which are prepared from cyclopentadiene and cyclopentanone or cyclohexanone (27, 270)). An interesting case is that of β-styrylfulvene (270), which contains both the fulvene and straight-chain butadiene structures: $C_6H_5CH=CH—CH=C(=C_4H_4)$. This compound could add maleic anhydride across either the cyclopentadiene ring or the butadienyl side chain, or both. Circumstantial evidence indicates that addition occurs across the ring, for the maleic anhydride adduct is dissociated in solution (270). A more stable adduct, which would involve the butadiene structure, might be formed at elevated temperatures. Formation of such an adduct appears to have been neither attempted nor reported.

E. Cyclohexadienes and cycloheptadienes

The liberation of an olefin and simultaneous formation of a benzene derivative on pyrolysis of adducts of acetylenic dienophiles with cyclohexadienes serves to distinguish cyclohexadienes from cyclopentadienes and cycloheptadienes (13). The test is not conclusive unless it is shown that both the olefin and the benzene derivative are formed, since the partially reduced adducts of acetylenedicarboxylic ester with furan or sylvan (2-methylfuran) and also the decarboxylated adduct of anthraquinone and maleic anhydride evolve ethylene on pyrolysis (14, 153). This property of evolution of olefins and formation of a benzene derivative is perhaps the most important chemical property of adducts of cyclohexadienes.

Cycloheptadiene adds acetylenedicarboxylic esters (14, 33) to give esters of 3,6-endopropylene-3,6-dihydrophthalic acid, which are either stable to heat or else decompose into their generators. Eucarvone (33, 357) is a cycloheptadienone; it adds maleic anhydride as follows:

Eucarvone
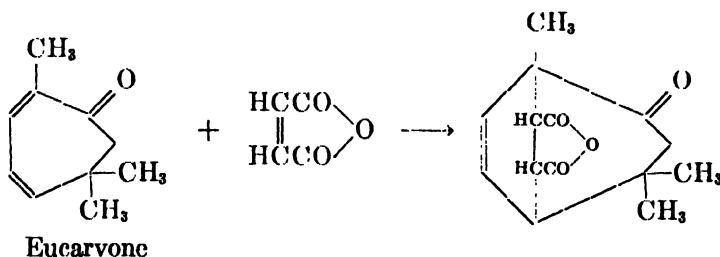
Cyclohexadiene additions have been rather well studied, though not as thoroughly as cyclopentadiene additions. Certain terpadienes, such as α-phellandrene, are conjugated cyclohexadienes. The decomposition of their acetylenedicarboxylic ester adducts to easily identified olefins and esters of phthalic acid and its homologs affords a convenient general method for structure determination of the original cyclohexadiene.

TABLE 5
Cyclohexadienes in the diene synthesis
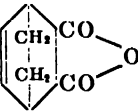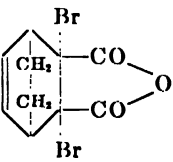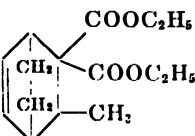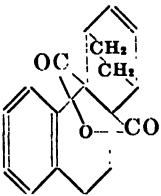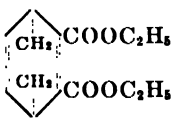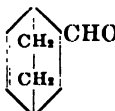
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Cyclohexadiene....	Maleic anhydride		(136, 146, 199)
Cyclohexadiene....	Dibromomaleic anhydride		(151)
Cyclohexadiene....	Ethylidenemalonic ester		(18)
Cyclohexadiene....	1,2-Dihydro-3,4-naphthalic anhydride		(213)
Cyclohexadiene....	Acetylenedicarboxylic diethyl ester		(13, 14, 147)
Cyclohexadiene....	Acrolein		(151)
Cyclohexadiene....	Benzoylethylene	No reaction	(47)
Cyclohexadiene....	*p*-Benzoquinone		(23, 153)

TABLE 5—*Continued*
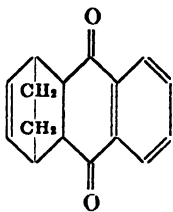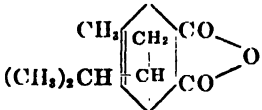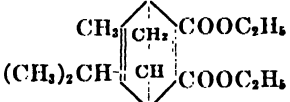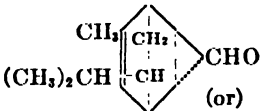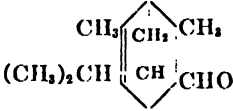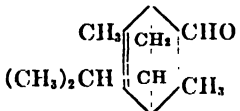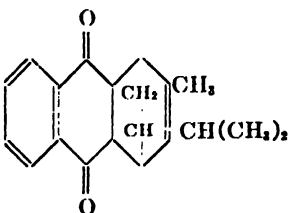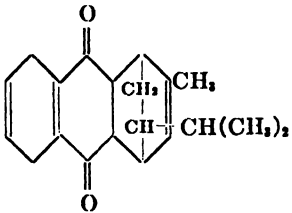
DIENE	DIENOPHILE	PRODUCT	REFERENCE
Cyclohexadiene....	α-Naphtho-quinone		(153)
α-Phellandrene	Maleic anhydride		(136, 418)
α-Phellandrene	Acetylenedicar-boxylic diethyl ester		(13)
α-Phellandrene	Acrolein	(or)	(144)
α-Phellandrene	Crotonaldehyde	or	(144)
α-Phellandrene ...	Benzoylethylene	"A hopeless mass"	(47)
α-Phellandrene	α-Naphthoquinone		(153)
α-Phellandrene	5,8-Dihydro-1,4-naphthoquinone		(135)

TABLE 5—*Continued*
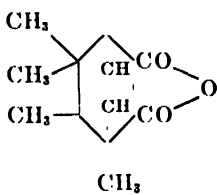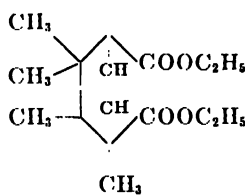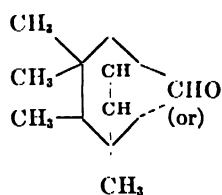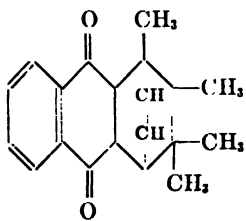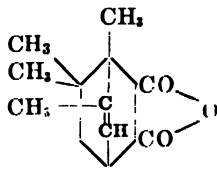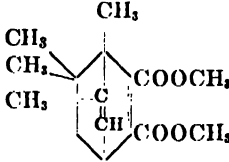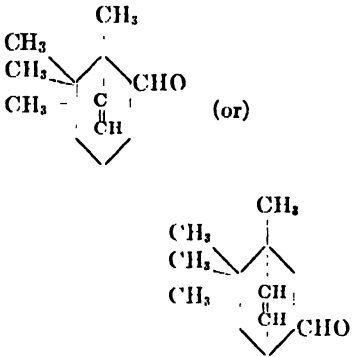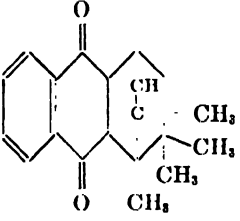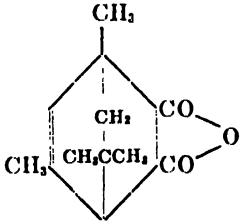
DIENE	DIENOPHILE	PRODUCT	REFERENCE
α-Pyronene........	Maleic anhydride	CH₃ / CH₃ / CH₃ — CH CO / CH CO O / CH₃	(190, 238, 407)
α-Pyronene........	Acetylenedicarboxylic dimethyl ester	CH₃ / CH₃ / CH₃ — CH COOC₂H₅ / CH COOC₂H₅ / CH₃	(191)
α-Pyronene........	Acrolein	CH₃ / CH₃ / CH₃ — CH CHO / CH (or) / CH₃	(190)
α-Pyronene........	Dibenzoylacetylene	No reaction	(191)
α-Pyronene........	*p*-Benzoquinone	No reaction	(191)
α-Pyronene........	α-Naphthoquinone	O CH₃ / CH—CH₃ / CH—CH₃ / CH₃ / O	(191)
β-Pyronene........	Maleic anhydride	CH₃ / CH₃ / CH₃ / CH₃ — C CO / CH CO O	(190, 407)

CH_3, CH, CO, $COOC_2H_5$, CHO

TABLE 5—*Concluded*

DIENE	DIENOPHILE	PRODUCT	REFERENCE
β-Pyronene........	Acetylenedicar-boxylic methyl ester		(191)
β-Pyronene........	Acrolein		(190)
δ-Pyronene........	Dibenzoyl-acetylene	No reaction	(191)
δ-Pyronene........	p-Benzoquinone	No reaction	(191)
δ-Pyronene......	α-Naphthoquinone		(191)
1,3,5,5,-Tetra-methylcyclo-hexadiene........	Maleic anhydride		(413)

β-Phellandrene, though not a cyclohexadiene, is isomeric with α-phellandrene, and differs from the latter only in double-bond arrangement. One of these double bonds is semicyclic and is conjugated with the other. Refluxing with

maleic anhydride (228) gives a resinous reaction product, high-vacuum distillation of which affords an 8 per cent yield of the adduct of α-phellandrene and maleic anhydride. This adduct could be detected only as the result of distillation and probably is formed on pyrolysis of the resin rather than by any direct interaction of maleic anhydride and β-phellandrene. This indicates that normal diene syntheses to *trans*-butadienoidal configurations do not occur without rearrangement, and is evidence for the rule given on page 323.

F. "Semicyclic" and dicyclic dienes

These include dienes such as 1-vinylcyclopentene and bis-1-cyclohexenyl. Of the first type, 1-vinylcyclohexene itself has been shown (126) to add maleic anhydride to give 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalic anhydride (IX) and to add *p*-benzoquinone to give 5,6,7,8,10,1a,4a,5a-octahydro-1,4-phenanthrenequinone (X) and also 1,1a,4,4a,5,5a,8,8a-*Bz*-(1,2,3,4)-*Bz'*-(1,2,3,4)-hexadecahydro-1,2,5,6-dibenz-9,10-anthraquinone (XI):

IX   X   XI
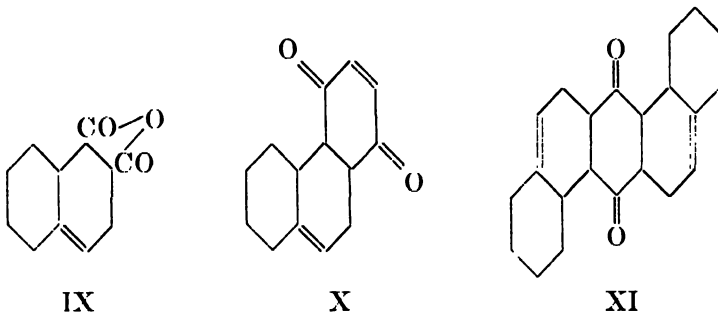
That these types of dienes are quite active is shown by the fact that 1-vinyl-2-methylcyclohexene adds maleic anhydride, cyclohexen-3-one, and crotonaldehyde (293) to give adducts XII, XIII, and XIV, respectively, all of which contain angular methyl groups.

XII   XIII   XIV
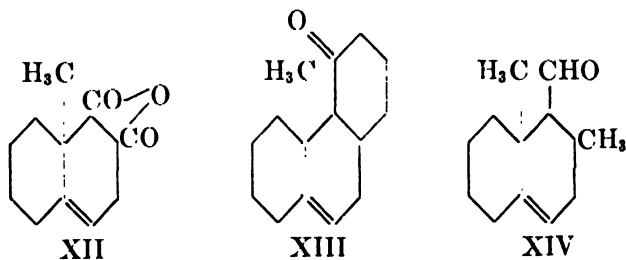
Bis-1,1'-cyclopentenyl (74) adds maleic anhydride to give the dicarboxylic acid (XV). In boiling methanol, *p*-benzoquinone adds 1 mole of the diene to give XVI; if the two compounds are boiled together for a minute or less (74), 2 moles of the diene are added to give XVII. α-Naphthoquinone adds 1 mole of the diene in boiling ethanol, giving XVIII.
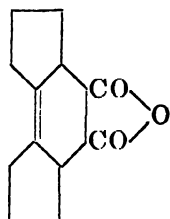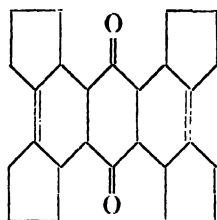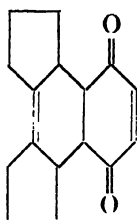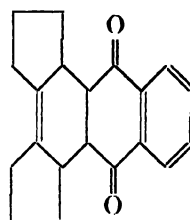
XV   XVI   XVII   XVIII

The corresponding compound with six-membered rings, bis-1-cyclohexenyl, adds maleic anhydride (5, 74, 232) to give the reduced 9,10-phenanthrene-dicarboxylic anhydride (XIX). Acrolein gives the reduced 9-aldehydophenan-threne (XX). p-Benzoquinone yields the reduced 9,10-benz-1,4-phenanthrene-quinone (XXI) (74) when the generators are dissolved in boiling ethanol. When the generators are boiled together without any solvent, the product is the reduced 1,2,3,4,5,6,7,8-tetrabenz-9,10-anthraquinone (XXII). α-Naphtho-quinone gives the reduced 1,2,3,4-dibenzanthraquinone (XXIII).
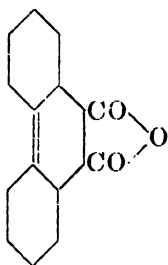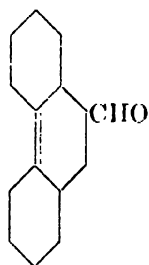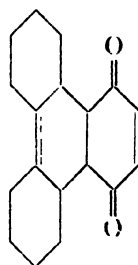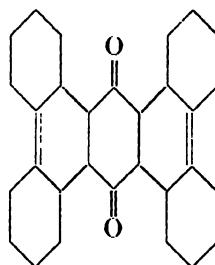
XIX   XX   XXI   XXII
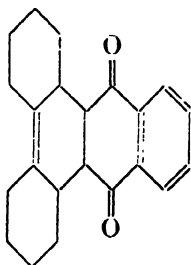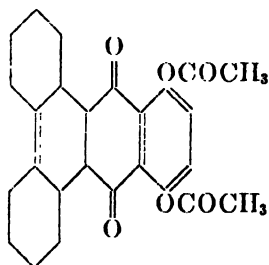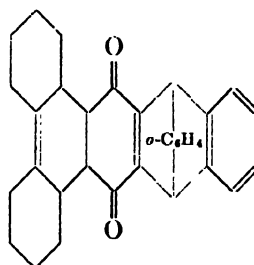
XXIII   XXIV   XXV
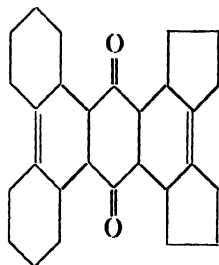
XXVI

Bis-1-cyclohexenyl is also added by naphthazarin diacetate (74) to give **XXIV**, and by 9,10-dihydro-9,10-endo-*o*-phenylene-1,4-anthraquinone (74) to give **XXV**. The quinone **XVI**, formed from bis-1-cyclopentenyl and *p*-benzoquinone in boiling methanol, will add a mole of bis-1-cyclohexenyl when the two are refluxed together (74), yielding **XXVI**.

Benzologs of the two above dienes have been studied. Bis-1-indenyl (340) has been shown to add maleic anhydride to give the reduced anhydride (**XXVII**), and 1,1'-bidialin (bis-3,4-dihydro-1-naphthyl) likewise gives the reduced anhydride (**XXVIII**). The bidialin addition does not take place as readily as does the bis-1-cyclohexenyl addition (297, 352). Barnett (74) reported failure to obtain a pure maleic anhydride addition product with bidialin, and stated that no reaction was observed between bidialin and *p*-benzoquinone or α-naphthoquinone.
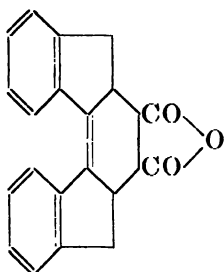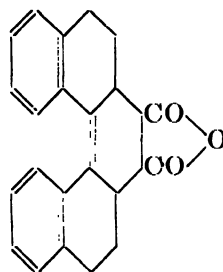
XXVII   XXVIII

Benzologs of 1-vinyl-1-cyclohexene have also been studied. 6-Methoxy-1-vinyl-3,4-dihydronaphthalene has been studied extensively, because the products formed are of importance in that they are preliminary products obtained in the rapidly developing field of sterol syntheses by diene reactions (93, 129, 130, 131, 132, 133). By choice of suitable dienophiles, adducts possessing the sterol-ring structure may be prepared, as shown in table 6.

The adduct of 2-methylcyclopenten-3,4-dione given in table 6 has been converted (132) into an isomer of estrone (**XXIX**)
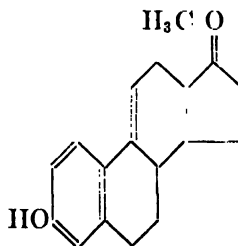
XXIX

The semicyclic enynes, 3,4-dihydro-1-naphthylacetylene and its 6-methoxy derivative, add ethylenic and acetylenic dienophiles; the latter type of dienophile gives derivatives of 9,10-dihydrophenanthrene as adducts. Propiolic acid (130) gives a mixture of 9,10-dihydrophenanthrene-1- and 2-carboxylic acids on reac-

TABLE 6
Diene syntheses of 6-methoxy-1-vinyl-3,4-dihydronaphthalene
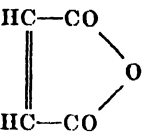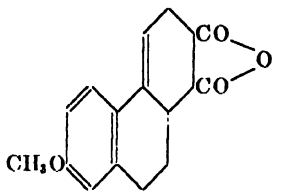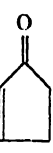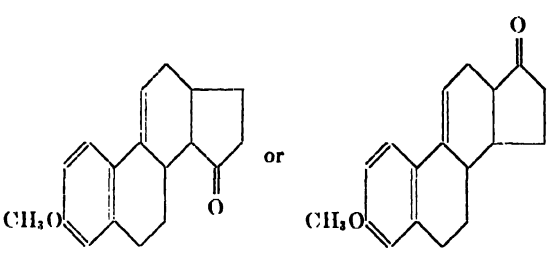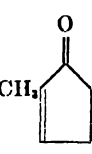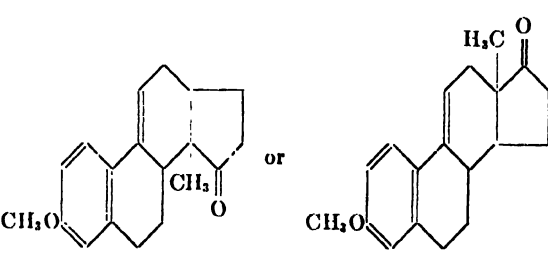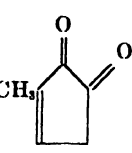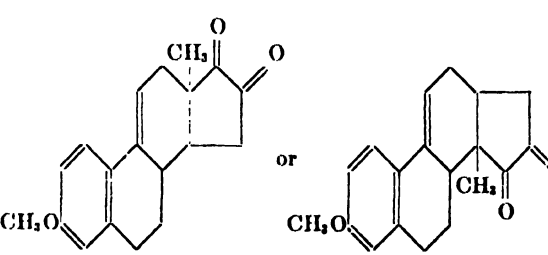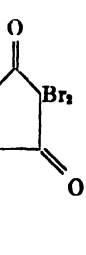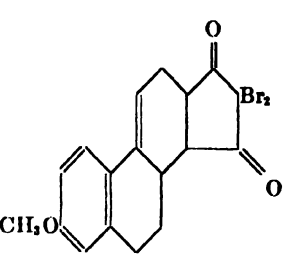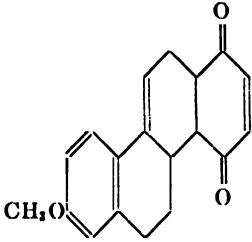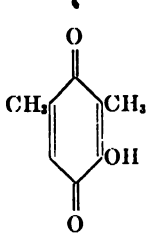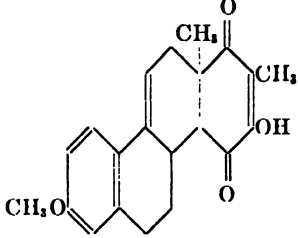
DIENOPHILE	PRODUCT

TABLE 6—*Concluded*

DIENOPHILE	PRODUCT

tion with 3,4-dihydro-1-naphthylacetylene, the 1-carboxylic acid being formed in greater amount.
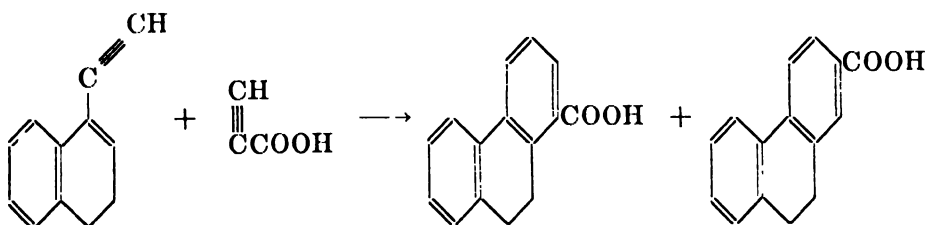
6-Methoxy-3,4-dihydro-1-naphthylacetylene adds propiolic acid (130) to give both **XXX** and **XXXI**. It does not add *p*-benzoquinone (130), but does add maleic anhydride (131), giving **XXXII**.
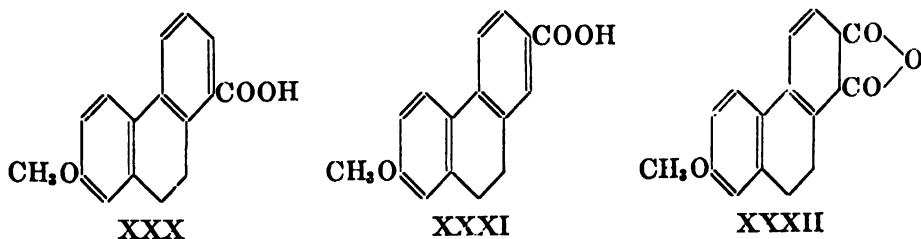
Since **XXXII** contains the 1,3-cyclohexadiene ring, it should be capable of adding further quantities of dienophiles. *p*-Benzoquinone does not add, but

interaction occurs (130) in which the quinone is reduced to hydroquinone and XXXII is converted into the anhydride of phenanthrene-1,2-dicarboxylic acid. The hydroquinone appears in the form of quinhydrone. On the other hand, maleic anhydride is added to give a bridged dianhydride (131):
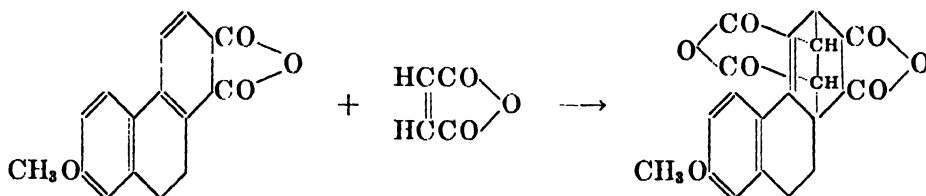
In this manner it may be seen that 3,4-dihydro-1-naphthylethylene and 3,4-dihydro-1-naphthylacetylene and their derivatives offer excellent possibilities as intermediates in the syntheses of the sterols and their derivatives. The reactions of the sterols themselves in the diene synthesis will be considered next.

VII. STEROLS

A. *Ergosterol and derivatives*

In the investigation of the various sterols and sterol derivatives from the standpoint of the diene synthesis, maleic and citraconic anhydrides have been almost the sole dienophiles employed. Certain of the irradiation products of ergosterol are active toward dienophiles. Lettré (282) indicates the successive formation of irradiation products as follows:
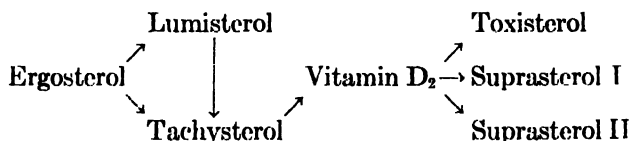
The use of acidic dienophiles in the investigations of the activities of the sterols in the diene synthesis is evident when one considers that the sterol adducts derived from such dienophiles are also acids. The adducts may therefore be separated from unchanged sterol simply by extracting with alkali, filtering from unchanged sterol, and precipitating with acid. Excess maleic or citraconic acid remains dissolved in the aqueous mother liquors.

Ergosterol adds maleic anhydride (282, 363, 366), best at a temperature of 135°C. Addition hardly occurs at room temperature and only slowly at 80°C. The same holds true for ergosteryl acetate (252, 366). The maleic anhydride adduct of ergosterol has structure I, and the corresponding adduct of ergosteryl acetate has a similar structure (253, 364). However, ordinary ergosteryl acetate shows only partial reaction with maleic anhydride (366), for a residue of dihydroergosteryl acetate remains unattacked. Distillation of the adduct of ergosteryl acetate and maleic anhydride in high vacuum gives maleic and succinic anhydrides, and a portion of the ergosteryl acetate may be recovered (366).

$$CH_3 \quad CH_3 \quad CH_3$$

CHCH=CHCHCH

CH₃ ... CH₃

CH₃

CH––CO

HO ––CH CO O

I
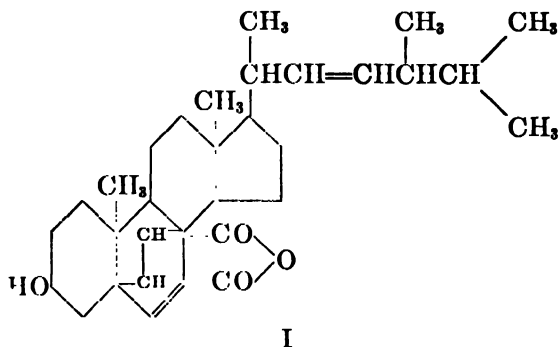
This recalls the formation of succinic anhydride and *p*-cymene by distillation of the adducts of maleic anhydride with α-phellandrene and with 1,3-menthadiene (page 388). Apparently a portion of the ergosteryl acetate appears as a dehydroergosteryl acetate, which probably possesses an aromatic ring. Reduction of the ergosteryl acetate–maleic anhydride adduct leads to initial hydrogenation of the double bond in the side chain. When ergosterol itself is reduced, the conjugated system is attacked first. By reduction of the ergosteryl acetate adduct and heating, 22-dihydroergosteryl acetate is produced, saponification of which gives 22-dihydroergosterol (364). 22-Dihydroergosterol, of course, adds maleic anhydride (362) to give a compound identical with I, except that the side chain is saturated. Windaus and Lüttringhaus (366) dispute this addition to a certain extent by saying that "dihydroergosterol" does not add maleic anhydride. There are three possible dihydroergosterols, only one of which has the conjugated-double-bond system required for the diene synthesis.

A tetrahydroergosteryl acetate (235) has been reported to add maleic anhydride. If this can be repeated, then the way is paved for an investigation of the mechanism of the reaction, for presumably the tetrahydroergosteryl acetate contains but one double bond.

Dehydroergosteryl acetate (235) adds maleic anhydride to give an adduct which appears to exhibit dimorphism. It may be distilled unchanged at 220°C. and in the cathode-glow vacuum (10⁻⁴ mm. of mercury), but decomposition into the generators occurs at 240°C. Dehydroergosterol itself also forms an adduct with maleic anhydride (234).

Tachysterol contains four double bonds and is formed from ergosterol on irradiation, when the central six-membered ring is opened. Lettré (282) suggests two alternative structures for the sterol, as shown below:

H₃C R H₃C R

H₃C H₃C

HO or HO

where R is

$$-CH(CH_3)CH=CHCHCH_3$$
$$\overset{|}{CH(CH_3)_2}$$
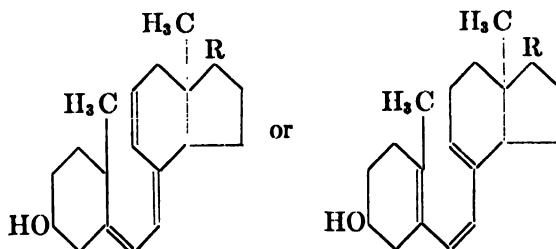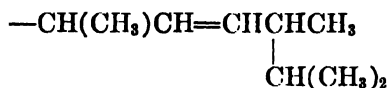
Lettré calls attention to the fact that, while ergosterol requires a temperature of 135°C. for the addition of maleic anhydride, tachysterol will add citraconic anhydride at room temperature (282). This adduct contains only two double bonds and its formation is interpreted as meaning that two molecules of citraconic anhydride have added, probably by addition of one molecule of citraconic anhydride followed by wandering of a double bond in the resulting product to give a conjugated system which then adds the second molecule of citraconic anhydride. It is difficult to understand how such a wandering could occur readily at room temperature, however.

The next product in the irradiation sequence is vitamin D_2 (calciferol). It and its acetate add maleic anhydride (296, 368). Calciferol, like tachysterol, possesses an isolated double bond and three conjugated double bonds. There have been no reports to the effect that calciferol adds two molecules of maleic anhydride, however.

Heating calciferol to 190°C. results in ring closure and disappearance of a double bond with the formation of two isomeric products, isopyrovitamin and pyrocalciferol. Two double bonds are present in a single ring in each isomer, and each adds maleic anhydride (296).

Irradiated ergosterol was found to have lost its antirachitic power when treated with maleic anhydride or citraconic anhydride (367), thus indicating that vitamin D_1 contains conjugated double bonds. An earlier observation (361) indicated that maleic anhydride would not react with irradiated ergosterol, which led to the conclusion that the conjugated system of ergosterol is destroyed by irradiation. This is false, as was shown above.

The reaction of citraconic anhydride with irradiated ergosterol is incomplete, some 10 to 20 per cent remaining unattacked. The tachysterol which may be isolated from irradiated ergosterol reacts nearly as readily with citraconic anhydride (369) as it does with maleic anhydride.

Pure vitamin D_2 adds citraconic anhydride very slowly (365) and it is to be expected that the maleic anhydride addition proceeds more rapidly (368).

Windaus and Thiele (368) give the formula of calciferol as
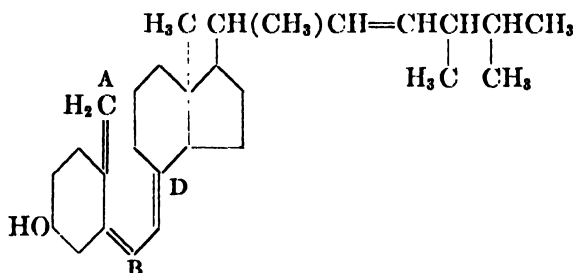
and they state that maleic anhydride adds to carbon atoms A and B rather than to B and D. If the latter addition did occur, a ring with gem-substitution (a spirane) would be formed. This reaction would be expected to be much slower than the reaction between maleic anhydride and the combination of A and B.

Windaus and Lüttringhaus (366) divide the ergosterol derivatives into three classes according to their abilities to add dienophiles. Class I compounds react readily with maleic anhydride on staining at room temperature for several days, and include tachysterol, dehydroergosterol, one of the three isoergosterols, and certain irradiation products of ergosterol. Class II compounds, comprising ergosterol and its acetate, barely exhibit reaction at room temperature but react readily at 135°C. Class III compounds show no reaction, and comprise a dihydroergosterol, ergosterols D and F, the other two isoergosterols, and the products of the over-irradiation of ergosterol.

When ergosteryl acetate is treated with hydrogen chloride, the reaction products may be separated to some degree through the use of maleic anhydride (360). The adducts are separated by solution in caustic alkali and are decomposed into their generators by heating in high vacuum.

B. Cholesterol and derivatives

Cholesterol derivatives have been investigated only slightly with regard to their abilities to add dienophiles. 2,4-Cholestadiene adds maleic anhydride readily in boiling xylene solution (339). The mixture termed "cholesterilene," –the main constituent of which is probably 3,5-cholestadiene,– adds maleic anhydride to some extent, but the product appears to be abnormal (194, 338). 3,5-Cholestadiene itself possesses a *trans*-butadienoidal configuration, and it adds maleic anhydride only under drastic conditions (338, 347). The product obtained is probably polymeric, for its alkali salts are insoluble in water (distinction from other sterol-maleic anhydride adducts). 2,4-Cholestadiene is claimed to give an abnormal addition product with maleic anhydride (194), although it contains the 1,3-cyclohexadiene ring. This claim has been disputed (339).

Coprastadienol (365) adds maleic anhydride easily to give an adduct which is best isolated in the form of the acetate by treatment of the adduct with acetic anhydride, since the adduct acetate crystallizes far better than does the original adduct.

$\Delta^{6,8(14)}$-Cholestadiene and $\Delta^{7,9(11)}$-cholestadiene possess *trans*-butadienoidal configurations; they do not add maleic anhydride (405). On the other hand, $\Delta^{7,14}$-cholestadiene possesses a *cis*-butadienoidal configuration and is able to add maleic anhydride.

VIII. TERPENES AND TERPINOID BODIES IN THE DIENE SYNTHESIS

The terpenes often react as dienes, and sometimes even if they do not contain conjugated double bonds. It is likely that isomerization takes place prior to

the consummation of the diene reaction; a somewhat satisfactory explanation can be advanced on this basis for most of the reactions.

Hultzsch (238) obtained addition of maleic anhydride to α-pinene, limonene, terpinolene, and 3-carene at reflux temperatures. None of the adducts appeared to be identical. On the other hand, when maleic acid was employed as dienophile, all the adducts were identical, and were the same as the adduct obtained from 1,3-p-menthadiene and maleic acid. Diels (162) observed that 3-carene[2] formed an adduct with maleic anhydride, which did not appear to be identical with the adduct from 1,3-p-menthadiene and maleic anhydride. He took the view that, inasmuch as the cyclopropane ring often acts as a double bond (as in the addition of hydrogen bromide or bromine to cyclopropane; see, however, Kharasch, Fineman, and Mayo (266)), the cyclopropane ring could function as a double bond and be in conjugation with the double bond of what he called 3-carene[2].
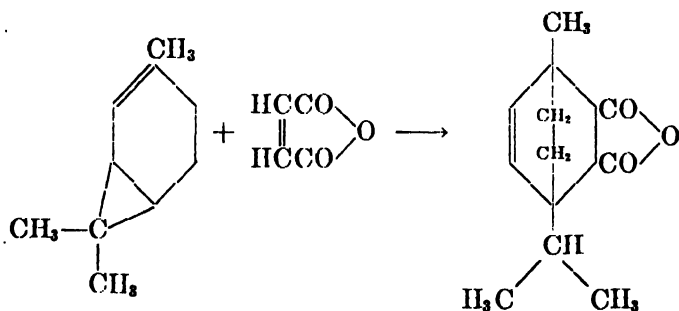
Diels apparently neglected to consider the equally likely mechanism:
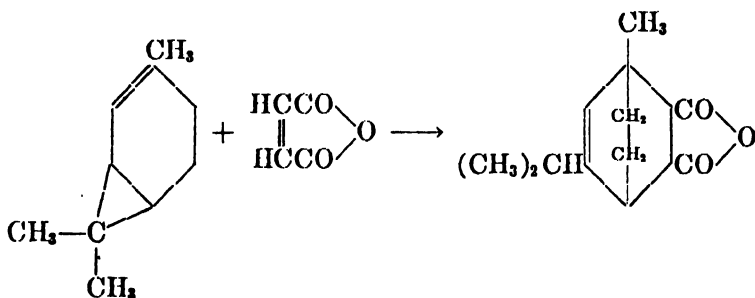
A somewhat more satisfactoy rexplanation for certain of these observations may possibly be found in the application of generally known facts of terpene

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[2] There is controversy in the literature regarding the carenes. Goodway and West (228) state that 3-carene does not contain a cyclopropane ring in conjugation with the double bond, while Hultzsch (238) states that Diels used 4-carene in his reaction. Hultzsch obtained addition with both 3-carene and 4-carene.

TABLE 7

The additions of maleic anhydride to dienic acids and their derivatives
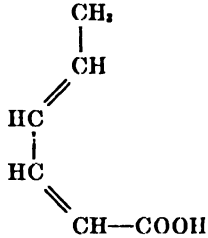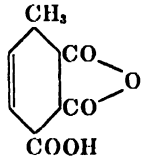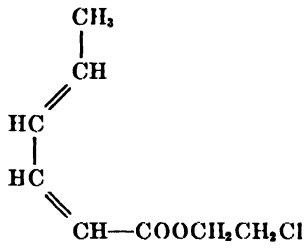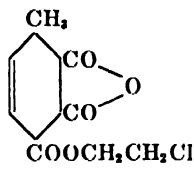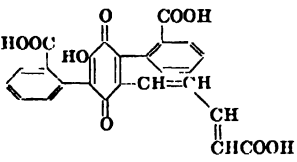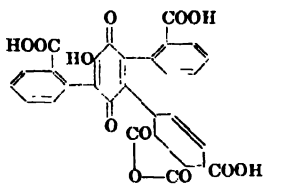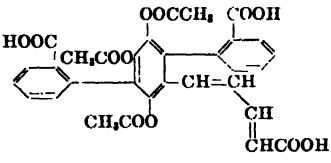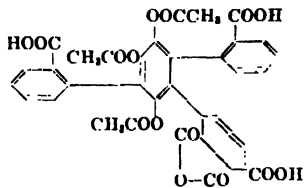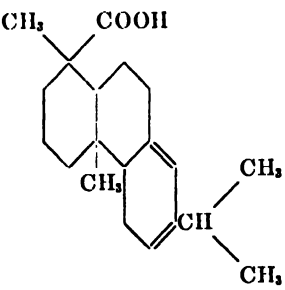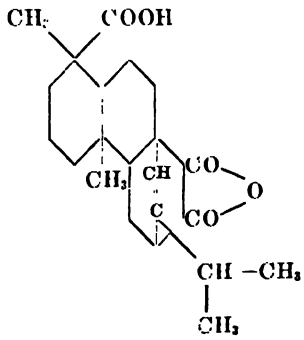
DIENE	DIENE STRUCTURE	PRODUCT STRUCTURE	REFER-ENCE
Sorbic acid			(199)
β-Chloroethyl sorbate			(347)
Muscarufin			(269)
Triacetylleuco-muscarufin			(269)
l-Pimaric acid			(69, 205, 317, 324, 359)

TABLE 7—*Continued*
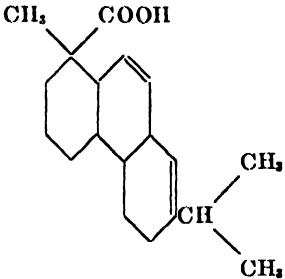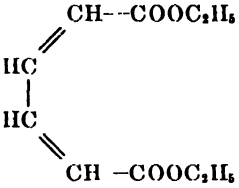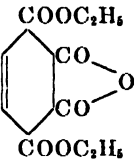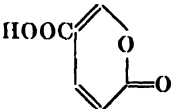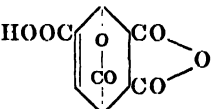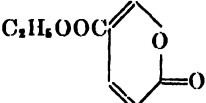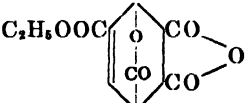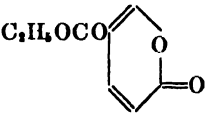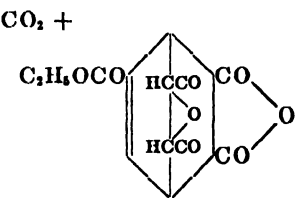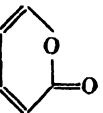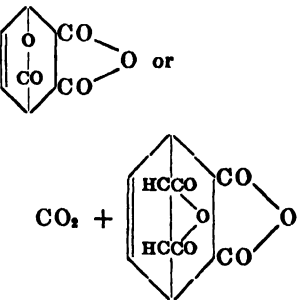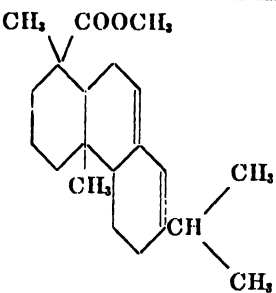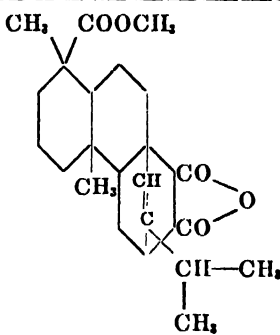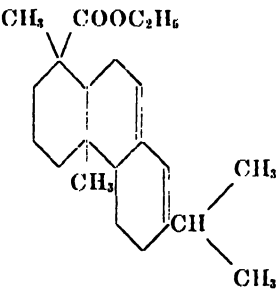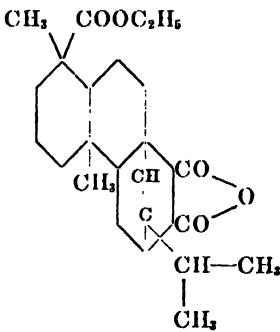
DIENE	DIENE STRUCTURE	PRODUCT STRUCTURE	REFERENCE
d-Pimaric acid...		Polymeric product	(314)
Ethyl *trans-trans*-muconate.			(199)
Cumalinic acid ..			(145)
Cumalinic ester (at 110°C.)			(145)
Cumalinic ester (at 138–140°C.).		CO_2 +	(145)
Cumalin.........		or CO_2 +	(145)

TABLE 7—*Continued*

DIENE	DIENE STRUCTURE	PRODUCT STRUCTURE	REFERENCE
Dimethylcumalin..........			(145)
Isodehydracetic acid..........			(145)
Spilanthole ...			(64)
Abietic acid*			(55, 314)

* Fieser's structure for abietic acid. Its adduct is identical with that obtained from *l*-pimaric acid.

TABLE 7—*Concluded*

DIENE	DIENE STRUCTURE	PRODUCT STRUCTURE	REFERENCE
Methyl abietate			(314)
Ethyl abietate			(314)

chemistry. The explanations here advanced fail when applied to the maleic anhydride additions, though they explain the maleic acid additions.

In the case of the pinene addition, it is known that α-pinene is transformed into terpineol when boiled with dilute acids, and also into α-terpinene and terpinolene simply by refluxing with clay (312):
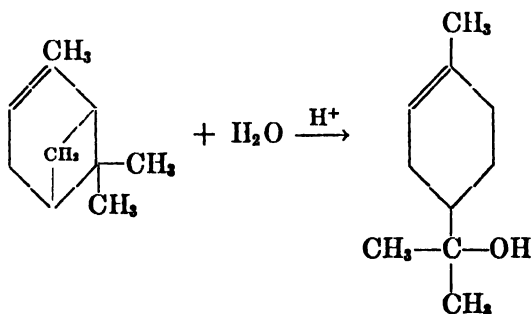
The tertiary alcohol can lose water and form *dl*-limonene or terpinolene. Alder and Rickert (15) obtained mostly 1,3-menthadiene by direct degradation:

$$CH_3 \quad \xleftarrow{-H_2O} \quad CH_3 \quad \xrightarrow{-H_2O} \quad CH_3$$

$$C \qquad CH_3-\overset{|}{C}-OH \qquad CH_3-C-CH_3$$

$$CH_3 \quad CH_2 \qquad \overset{|}{CH_3}$$

$$\xrightarrow{-H_2O} \qquad CH_3$$

$$CH_3-CH-CH_3$$
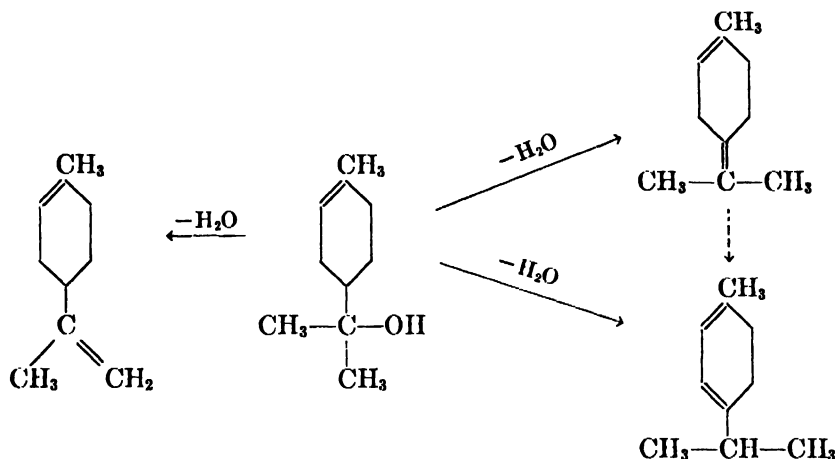
Semicyclic double bonds such as exist in terpinolene wander into the ring under the influence of acids. In this manner terpinolene gives terpinene (1,3-*p*-menthadiene) very readily with dilute acid. Dilute acids also transform terpineol into terpinolene, *dl*-limonene, or 1,3-*p*-menthadiene, depending on the conditions. Alcoholic sulfuric acid will convert limonene into 1,3-*p*-menthadiene.

Heat alone will convert α-pinene into 1,3-*p*-menthadiene, accounting for the observation of Hultzsch (237) that high-temperature turpentine reacts more thoroughly with maleic anhydride than does low-temperature turpentine. Since an acid medium (due to maleic anhydride or maleic acid) exists in the α-pinene diene synthesis, the following sequence of reactions is likely:

$$CH_3 \qquad \xrightarrow[\text{anhydride}]{\text{maleic}} \qquad CH_3$$

$$\overset{|}{CH} \qquad\qquad CH$$

$$H_3C \qquad CH_3 \qquad H_3C \qquad CH_3$$

$$CH_3 \quad\longrightarrow\quad CH_3 \quad\longrightarrow\quad CH_3 \quad\longrightarrow\quad CH_3$$

$$CH_3-\overset{|}{C}-OH \qquad CH_3-C-CH_3 \qquad C$$

$$\overset{|}{CH_3} \qquad\qquad\qquad H_3C \qquad CH_2$$
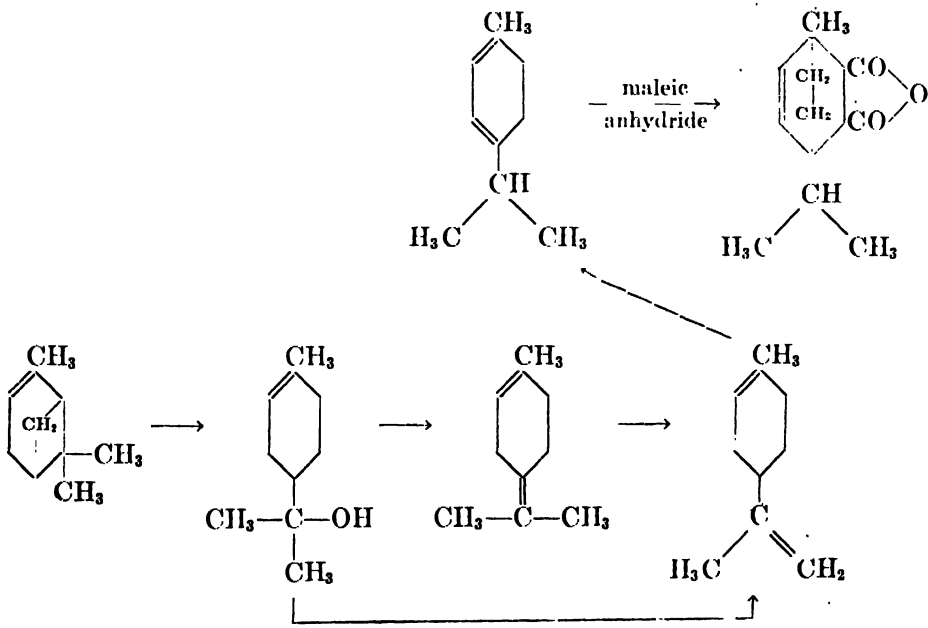
Since limonene and terpinolene are intermediates in the transformation of α-pinene to 1,3-*p*-menthadiene, their reactions with maleic acid are obvious. Support for this mechanism is furnished by the observation (226) that terpinolene and γ-terpinene do not add maleic anhydride at room temperature.

3-Carene (4-carene) is easily isomerized by dilute acids to a mixture of *dl*-limonene and sylvestrene:
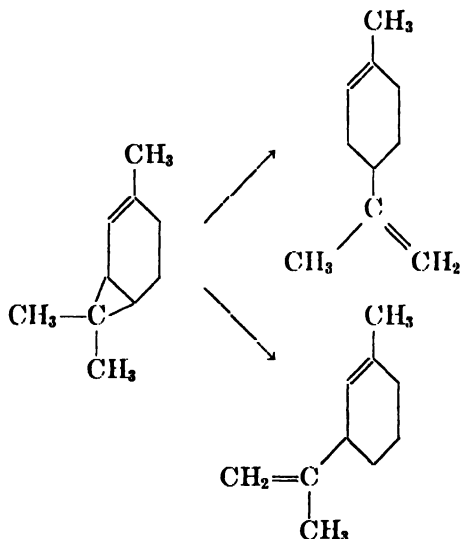
It may be that sylvestrene is convertible into 1-methyl-3-isopropyl-1,3-cyclohexadiene by acids, though it is one of the most stable of the terpenes. According to this view the 3(or 4)-carene adduct with maleic anhydride is a mixture of I and II:

I   II
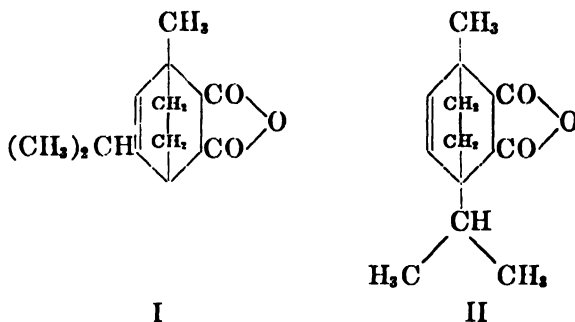
This view does not take cognizance of the report that the maleic acid adduct of 3(or 4)-carene is identical with the adducts of the other three terpenes. It would be indicated that at the hydrogen-ion concentration furnished by maleic acid, conversion of 3-carene or 4-carene to sylvestrene is at a minimum and that nearly all conversion is to *dl*-limonene. Since maleic anhydride would

scarcely be expected to be more acidic than maleic acid, it would follow that sylvestrene formation does not occur with maleic anhydride.

Arbuzov (56, 57; see also 388) passed α-pinene over copper chromite. At 300°C., a mixture of 80 per cent α-pinene and 20 per cent alloöcimene was obtained, while at 375°C. the composition was 23 per cent α-pinene, 31 per cent alloöcimene, and 12 per cent *dl*-limonene, whilst at 400–410°C., the composition was 20 per cent α-pinene, 23 per cent *dl*-limonene, 20 per cent alloöcimene, and 36 per cent of an unidentified terpene. Contrary to Arbuzov (388), β-pinene similarly yields alloöcimene.

Slobodin (332) has isomerized limonene and vinyl-3-cyclohexene by passage over floridin at 210–240°C. Limonene isomerized easily but vinylcyclohexene was more resistant. The isomerization products of each reacted vigorously with maleic anhydride. It was postulated that vinylcyclohexene isomerized to ethylidene-2-cyclohexene, but the presence or absence of other aromatics was not demonstrated or stated. No proof was given for the structures of the isomerizates.

Diels and Alder and their students (8, 15, 162) and Tischchenko and Bogomolov (342; see also 230) showed that α-terpinene added maleic anhydride. Diels and Alder (8, 15, 162), by reaction with acetylenedicarboxylic ester and then deolefinization of the adduct, proved that α-terpinene was 1,3-*p*-menthadiene.
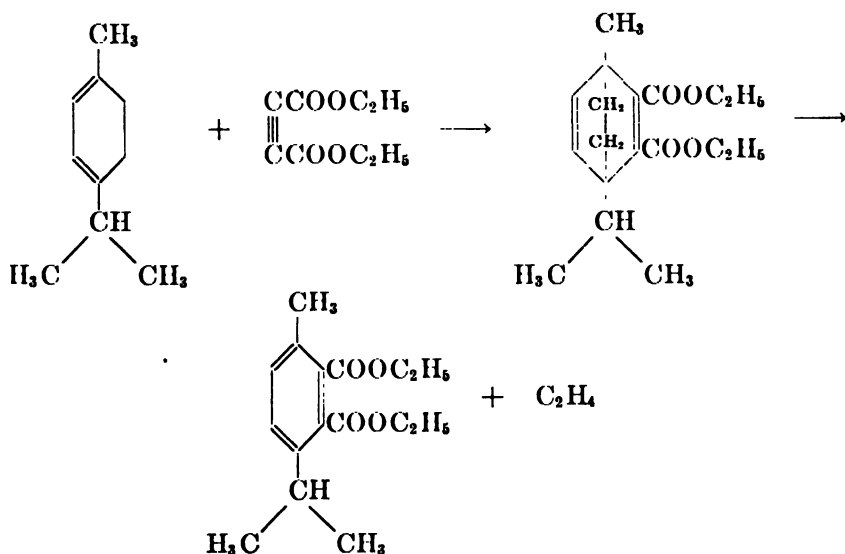

A second terpene was produced in addition to α-terpinene when terpineol was dehydrated (15). This contained conjugated double bonds, for it added acetylenedicarboxylic ester easily. This adduct did not decompose on distillation; hence the terpene is not a cyclohexadiene derivative. Alder and Rickert (15) feel that the material is a cycloheptadiene, and for circumstantial evidence they indicate von Baeyer's (70) carvone hydrobromide reaction:
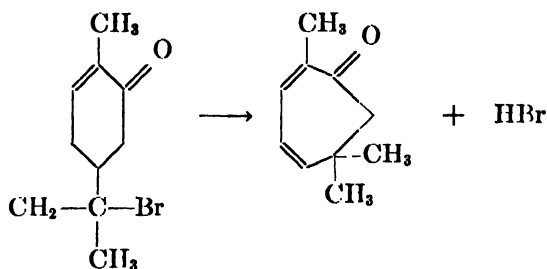
The cycloheptadienone is eucarvone. In accordance with this reaction, they believe their terpene to be eucarvene. Prior to this study, it had been generally believed that "terpinene" derived from terpineol was a mixture of 1,3- and 1,4-*p*-menthadienes.

Acrolein has been reported (342) to "add" to *dl*-limonene to give "a liquid which gives *dl*-limonene on distillation at atmospheric pressure."

A few more instances are available of diene reactions of terpinoid bodies which do not contain conjugated double bonds (284). These terpinoid bodies are interesting in that they contain no unsaturated linkages whatever, yet give diene reactions. These are the so-called nopinols,
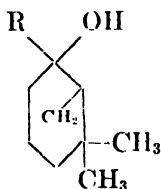
in which R may be hydrogen or alkyl. When R is hydrogen, the adduct I is obtained with maleic anhydride. This is the same as obtained from apo-α-terpinene (II). There is also obtained a material which is probably nopinyl maleate or fumarate, and a residue of probably the same composition. When R is methyl, the exclusive product of the reaction is III, which was obtained from α-pinene, terpinolene, 3(4?)-carene, α-terpinene, and *dl*-limonene with
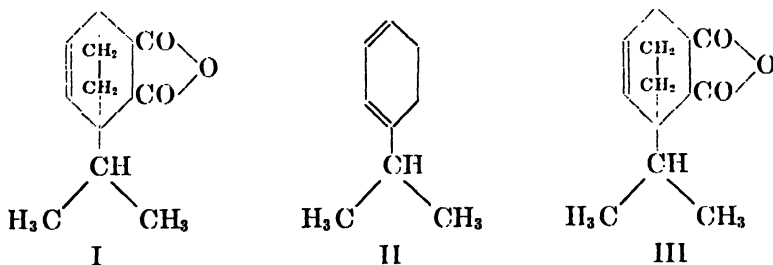

maleic acid. Similar products are obtained when R is phenyl or benzyl. The difficulty in obtaining a clean-cut reaction with nopinol may be attributed to the fact that when R is hydrogen, the material is a secondary alcohol, but when

R is an alkyl or aryl group, the material is a tertiary alcohol. Evidently one of the first steps in the process of addition is the elimination of water to form norpinene, pinene, or a related compound dependent on the identity of R. It will be recalled that secondary alcohols are dehydrated less readily than are tertiary alcohols; hence the difficulty when R is hydrogen. The sequence of reactions appears to be
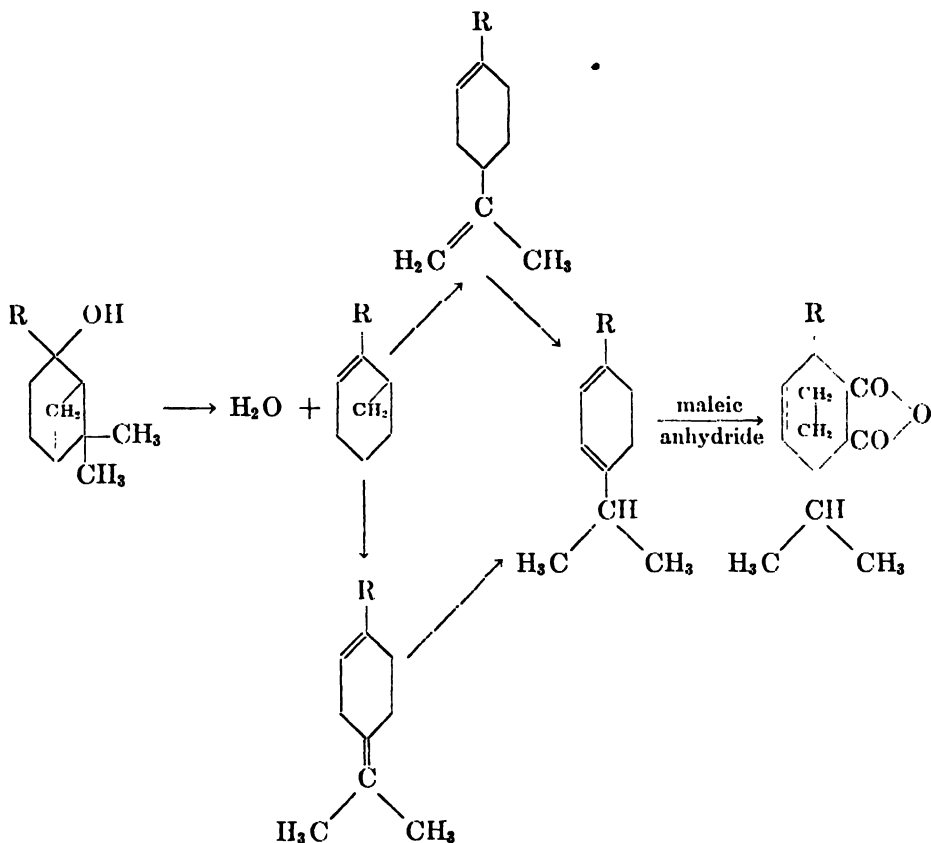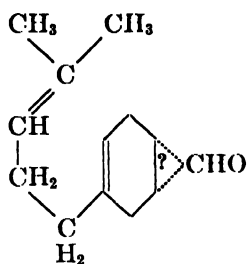

von Baeyer's eucarvone (70) has been observed to add maleic anhydride (33, 353) and acetylenedicarboxylic ester (15) (see page 404).
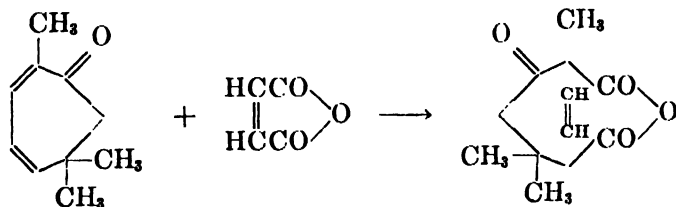
Myrcene has been found to add maleic anhydride (144, 313, 407), acrolein (139), and α-naphthoquinone (224) giving IV, V, and VI, respectively.
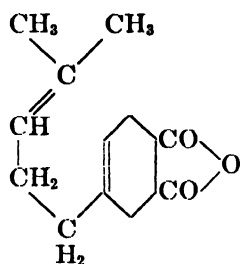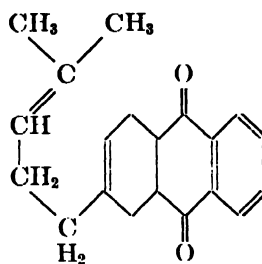
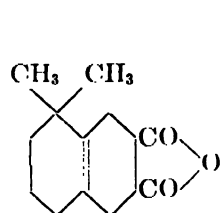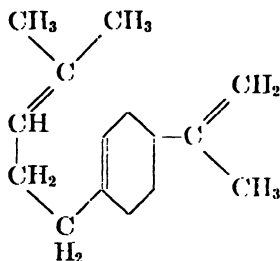IV   V   VI

Bromine water (144) or formic acid (313) will cyclize the maleic anhydride adduct to an octalin derivative (VII). This cyclizate yields 2,3,8-trimethylnaphthalene on dehydrogenation (313).
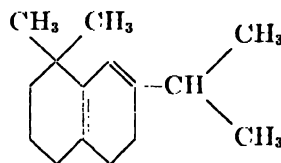
Isoprene will add to myrcene (315, 329) to give the so-called cycloisoprene-myrcene (VIII). Semmler and Jonas (329) observed this reaction as early as

VII   VIII   IX

1913 and found that *dl*-limonene is also produced (by dimerization of the isoprene). VIII cyclizes with formic acid (315) to give IX, the double-bond wandering being quite likely because of the acid conditions of the cyclization reaction. Dehydrogenation of the cyclizate gives eudalene.

Menogene (2,4(8)-*p*-menthadiene) is an example of a terpene containing a conjugated semicyclic double bond in the *trans*-butadienoid configuration. This adds maleic anhydride (236) to give an adduct, presumably X; but the conditions of the reaction, together with the fact that addition actually occurred, may well lead one to wonder if the semicyclic double bond had not wandered into the ring before addition actually occurred. At least a portion of the product may be the maleic anhydride adduct of 1,3-menthadiene or of 2,4(5)-menthadiene.
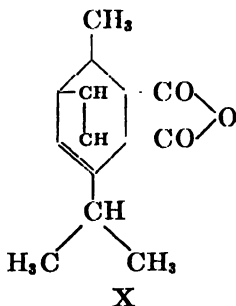

X

At least one quinone has been reacted with terpenes other than α-phellandrene (see the section on homocyclic dienes for α- and β-phellandrenes), and this is the reaction of naphthazarin with alloöcimene (59). The hydrocarbon has also been caused to react with maleic and citraconic anhydrides (56, 57, 238, 407). It is of interest to note that the melting points of the adducts of alloöcimene with maleic and with citraconic anhydrides are almost identical (56, 57).

As might have been expected, neither camphene nor camphor reacts with maleic anhydride (238). If the semicyclic double bond of camphene were to wander into the ring (this is unlikely, inasmuch as compounds of the type represented by XI are unknown in terpene chemistry and are unstable with respect to compounds of the type represented by XII), it is still a matter of some difficulty to understand just how rupture of the endomethylene bridge could possibly occur so as to give another double bond required for a conjugated system.
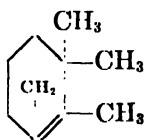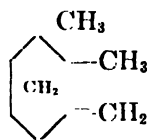

XI   XII

Ruzicka and Zimmermann (318) observed that the mixture of sesquiterpenes known as caryophyllene reacts with maleic anhydride to give a 70 per cent yield of adduct. At the time (1935) the formula of the main constituent of caryophyllene was given as XIII. In order to account for the formation of an adduct which appeared to be saturated (unattacked by ozone, alkaline permanganate, perbenzoic acid, or tetranitromethane), they assumed addition of maleic anhydride to the isolated system of double bonds, followed by cyclization, giving the compound XIV. If true, this would be a singular example of an anomalous diene reaction. A revised formula (XV) given in 1936 (reference
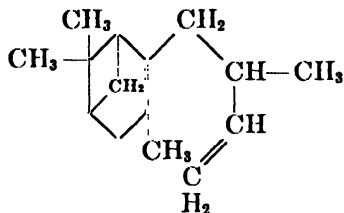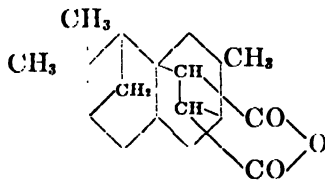

XIII   XIV
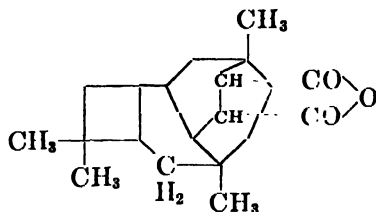
XV

319) appeared to state the case no more satisfactorily. In 1938, Rydon (320) proposed that the main constituent of caryophyllene is a cycloheptene deriva- tive (XVI), and that the maleic anhydride adduct is formed from a conjugated isomer (XVII). Since an alternative isomer (XVIII) is a *trans*-butadienoidal compound, it should hardly be expected to add maleic anhydride. Goodway and West (229) made a number of comments on the problem, among which was that absorption-spectrum studies of caryophyllene indicate the absence of any appreciable quantity of conjugated dienes. They also stated that if Rydon is correct, then the double bond of the adduct is highly unreactive, as it is in many terpinoid substances, since the apparently saturated nature of the adduct has been demonstrated. They finally concluded that the adduct is not formed by the diene synthesis.
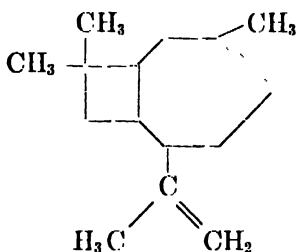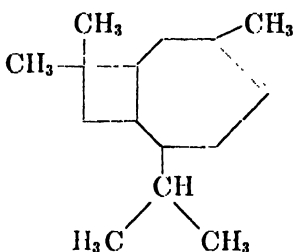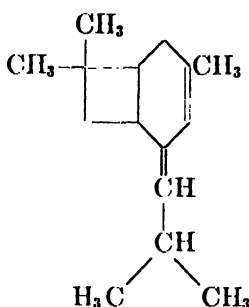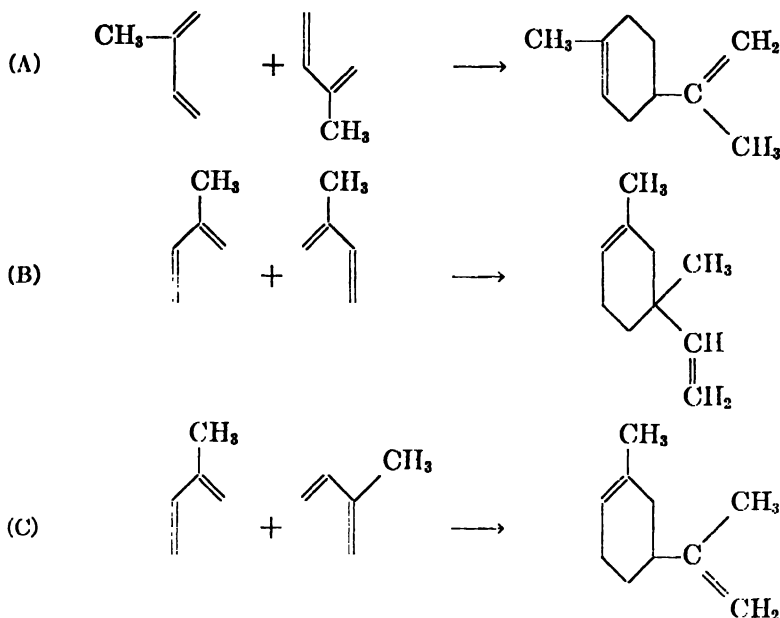

XVI   XVII   XVIII

IX. DIMERIZATION

A number of dimerization reactions of the type which may be represented by the diene synthesis had been discovered half a century or more ago. Repre- sentative of those observed around the beginning of the twentieth century is that of Wallach (349) who, in the year 1895, synthesized *dl*-limonene by dimeriza- tion of isoprene in the absence of oxygen and peroxides and employed elevated temperatures. Diels and Alder (136) considered this as a type of diene syn- thesis and extended the reaction to other dienic hydrocarbons. In many in- stances there were obtained trimers, tetramers, and pentamers. It was found that an elevated temperature is generally necessary to bring about dimerization, and an antioxidant such as hydroquinone or catechol is beneficial in elimination of the catalytic effects of peroxides on polymerization reactions which lead to the formation of polymers of high molecular weights.

Diels and Alder (136) postulated that the formation of *dl*-limonene occurred according to reaction A. Lebedev (275) thought that the geminal compound 1-vinyl-1,3-dimethyl-3-cyclohexene (reaction B) was formed at room tempera- ture; but later Wagner-Jauregg (345) found that while isoprene forms *dl*-limo- nene at high temperatures, the product formed at room temperature was diprene (reaction C):

(A) CH_3—[diene] + [diene]CH_3 ⟶ CH_3—[cyclohexene ring]—C(=CH_2)CH_3

(B) [diene CH_3] + [diene CH_3] ⟶ [cyclohexene ring CH_3, CH_3, CH=CH_2]

(C) [diene CH_3] + [diene CH_3] ⟶ [cyclohexene ring CH_3, C(=CH_2)CH_3]

Absence of products resulting from reaction B is in harmony with the general observations concerning optional additions of dienophiles. These are explained in greater detail on page 329.

In extension of the diene synthesis to the dimerizations of other hydrocarbons, it was found that butadiene gave vinyl-3-cyclohexene (16, 276, 334) when heated at 180°C. with hydroquinone:

$$CH_2\!=\!CH\!-\!CH\!=\!CH_2 \;+\; CH_2\!=\!CH\!-\!CH\!=\!CH_2 \;\longrightarrow\; \text{[vinylcyclohexene]}$$
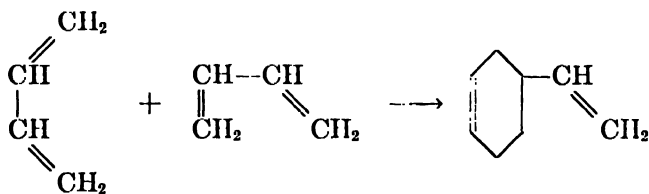
The product (vinylcyclohexene-3 or 4-vinylcyclohexene) does not add dienophiles, and therefore any proposed structure containing a conjugated system is unlikely. Dehydrogenation gives ethylbenzene; styrene may also be formed. Vinylcyclohexene-3 can add butadiene at elevated temperatures under antioxidant conditions to give butadiene trimer, which is 1,2,3,6,1′,2′,5′,6′-octahydrobiphenyl:

$$\text{[vinylcyclohexene]} \;+\; \text{[butadiene]} \;\longrightarrow\; \text{[octahydrobiphenyl]}$$
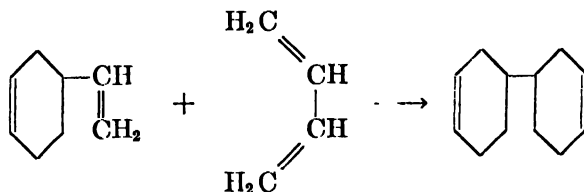
The fact that the trimer gives diphenyl on dehydrogenation establishes its ring structure and also affords strong evidence for the presence of a double bond on the side chain of the dimer. This evidence couples with the fact that the dimer does not react with dienophiles to show that the structure of vinylcyclohexene fits the facts best.

Vinylcyclohexene-3 will add other dienes as well as butadiene. Cyclopentadiene is added to give 1,2,3,6,1',2',5',6'-octahydro-3,6-endomethylene-biphenyl:
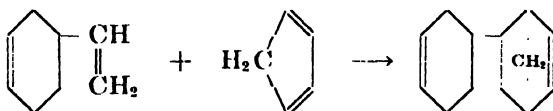

A considerable amount of α-tricyclopentadiene was formed in the above diene synthesis. The term "α-tricyclopentadiene" is a misnomer; it and similar names should be construed as meaning the trimer of cyclopentadiene.

1,2,3,4-Tetramethylbutadiene (311) has been observed to dimerize to the corresponding octamethyl-4-vinylcyclohexene.

Pirsch (302) discusses the various possible structures of the dimer of cyclopentadiene. This dimer is often referred to as dicyclopentadiene, especially in the older literature. Alder and Stein published a series of papers dealing with the proof of structure of this and other polymers, making a number of observations which led to deduction of their structures. Apparently the dimerization of cyclopentadiene is a true diene synthesis (135), proceeding as follows:
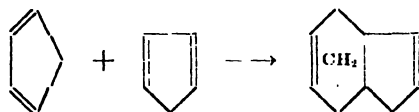
The degradation of the dimer to cyclopentane-1,3-dicarboxylic acid was accomplished in the following sequence of reactions: Partial hydrogenation of the dimer gives I, oxidation of which gives 3,6-endomethylenehexahydrohomophthalic acid (II). Further oxidation of II gives cyclopentanedicarboxylic acid (III). Such a degradation renders structure IV for the dimer inadmissible.
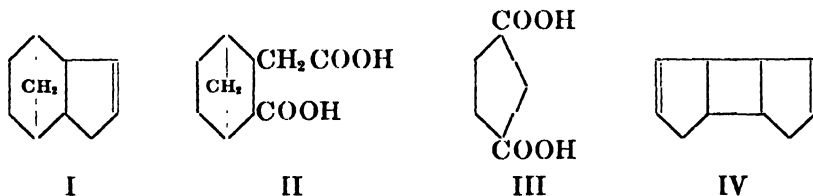
The dimer may be degraded to cyclopentane-1,3-dicarboxylic acid by another route (34):
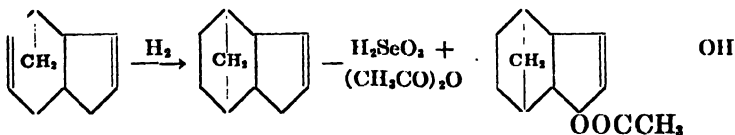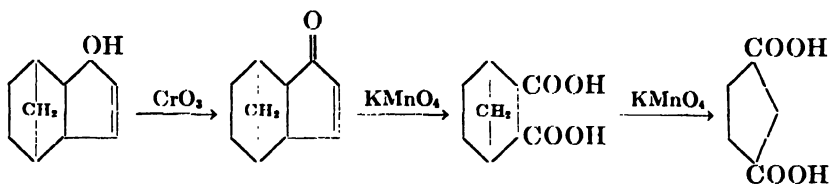
The reaction of phenyl azide with the double bond of the bicycloheptene ring appears to be rather specific, and was much used by Alder and Stein as a test for the presence of this ring in cyclopentadiene polymers. The test is not limited to detecting this ring in the polymers of cyclopentadiene, for the adducts of maleic anhydride and other dienophiles with cyclopentadiene give this test as well as does cyclopentadiene dimer or trimer (31). The evidence is strong for the presence of the bicycloheptene (3,6-endomethylenecyclohexene) ring in the dimer. The trimer also contains the bicycloheptene ring, as indicated by the phenyl azide reaction, and also by degradation of the trimer (31, 36) to a 3:3:0-bicyclo-octanetetracarboxylic acid by methods analogous to those used in the degradation of the dimer:
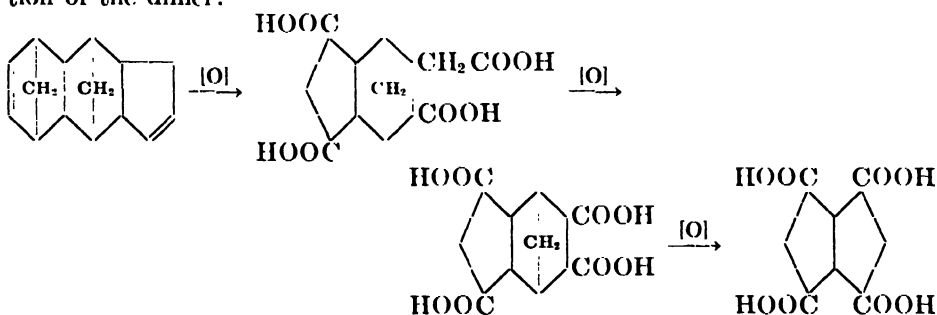
The double bond of the bicycloheptene ring is much more reactive than the other double bond of the dimer. Selective hydrogenation of this bond is accomplished with ease, and nitrosyl chloride adds to this bond rather than to the other. It would seem logical, therefore, that when the dimer adds another mole of cyclopentadiene to form the trimer, the reactive double bond is involved. This is indeed the case.

The dimer exists in two stereoisomeric forms, owing to the presence of the endomethylene group (29). The endo-isomer has the methylene group and the five-membered ring on opposite sides of the cyclohexene ring, whereas the exo-isomer has these on the same side. These are illustrated in the three-dimensional sketches below:
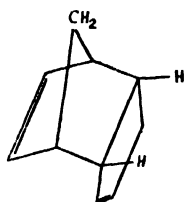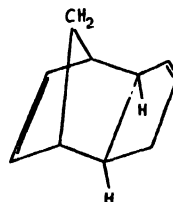
endo   exo

Addition takes place between two molecules of cyclopentadiene to give the endo-form, according to the general rules of stereochemical addition of dienes discussed in a later section (see page 497).

Since the trimer, tetramer, pentamer, etc., of cyclopentadiene are all formed by a series of diene syntheses involving the active double bond of the bicyclo-heptene ring as the "carbonylenic" double bond (though no carbonyl group is present, this term is used to denote the dienophilic double bond), the structures of these compounds are V, VI, and VII, respectively, in which all the endo-methylene groups lie on one side of the six-membered ring system and the unsaturated terminal five-membered ring lies on the other side of that ring system.
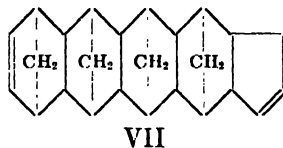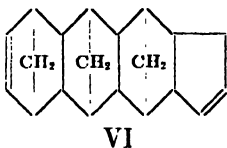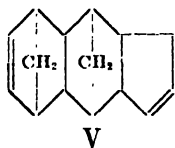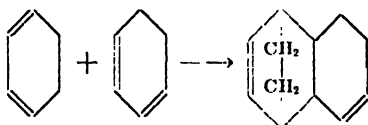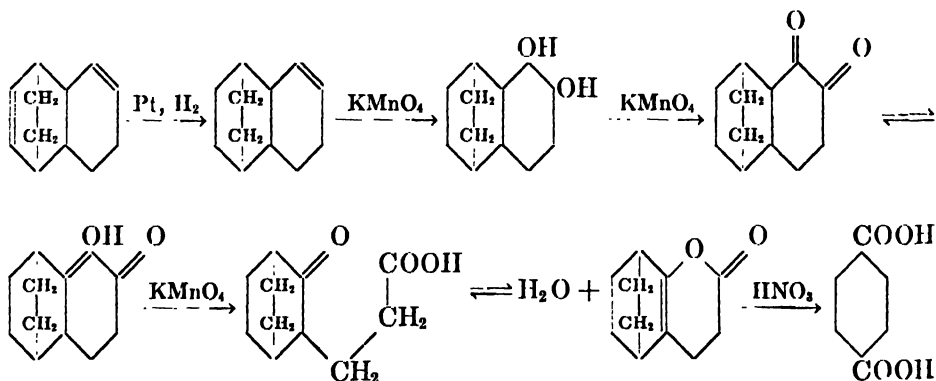
$$\underset{\text{V}}{\boxed{\text{CH}_2 \quad \text{CH}_2}} \qquad \underset{\text{VI}}{\boxed{\text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2}} \qquad \underset{\text{VII}}{\boxed{\text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2}}$$

Cyclohexadiene dimerizes in a manner similar to that of cyclopentadiene (22, 46). When considered as a diene synthesis, the product would be of the structure indicated by the reaction

$$\boxed{} + \boxed{} \longrightarrow \boxed{\text{CH}_2 \quad \text{CH}_2}$$

The structure of the product was elucidated (22) by a series of reactions as indicated in the scheme below, giving cis-hexahydroterephthalic acid as final product:

$$\boxed{\text{CH}_2 \; \text{CH}_2} \xrightarrow{\text{Pt, H}_2} \boxed{\text{CH}_2 \; \text{CH}_2} \xrightarrow{\text{KMnO}_4} \boxed{\text{CH}_2 \; \text{CH}_2}^{\text{OH}}_{\text{OH}} \xrightarrow{\text{KMnO}_4} \boxed{\text{CH}_2 \; \text{CH}_2}^{\text{O}}_{\text{O}} \rightleftarrows$$

$$\boxed{\text{CH}_2 \; \text{CH}_2}^{\text{OH} \; \text{O}} \xrightarrow{\text{KMnO}_4} \boxed{\text{CH}_2 \; \text{CH}_2}^{\text{O}} \underset{\text{CH}_2}{\overset{\text{COOH}}{|}} \rightleftarrows \text{H}_2\text{O} + \boxed{\text{CH}_2 \; \text{CH}_2}^{\text{O} \; \text{O}} \xrightarrow{\text{HNO}_3} \underset{\text{COOH}}{\overset{\text{COOH}}{\boxed{}}}$$

Kharasch and Sternfeld (268) prepared 1,3,5-hexatriene by the reaction of allyl chloride with a solution of sodium amide in liquid ammonia. This was found to dimerize to give VIII, the structure of which was proved.
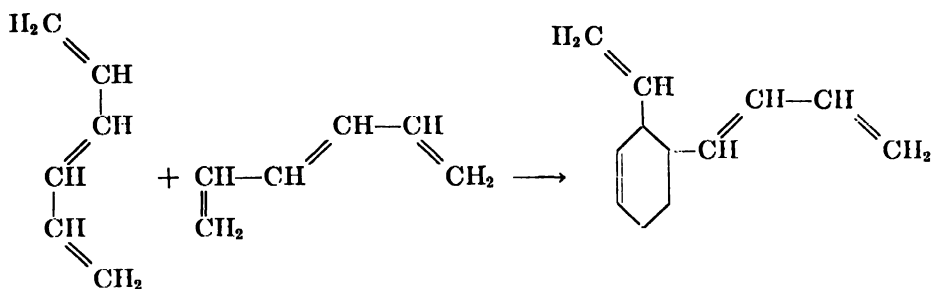
VIII

Since the dimer possesses a pair of conjugated double bonds, it adds maleic anhydride:
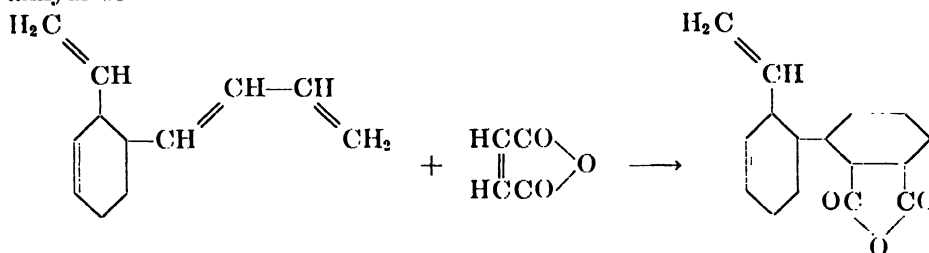
Hexatriene was also found to form a trimer and a tetramer, IX and X, respectively, the structures of which were postulated but not proved:

IX

X

It should be evident that there are several means whereby trimerization and tetramerization may occur. It is quite possible for trimerization to occur according to the scheme:

This trimer might undergo self-stabilization through an intramolecular diene reaction:

It may be seen, therefore, that in the absence of structural proof, the structures of hexatriene trimer and tetramer as postulated by Kharasch and Sternfeld are open to question.

According to Farmer (197), sorbic ester dimerizes at 230°C. to give three isomeric dimerides, which are cyclohexene derivatives. A trimeride is also formed, but this is so insoluble in the monomer–dimer mixture that no appreciable amounts of tetramer are formed. Kuhn and Deutsch (272) state that only one dimer is formed and that its structure is that of XI.

XI

1-Phenylbutadiene (**82**) appears to dimerize abnormally, since the dimer is not a cyclohexene derivative but is 1-(β-styryl)-2-benzyl-3-cyclopentene. This structure was proved by oxidation of the compound to benzoic and α-benzyltricarballylic acids. Farmer (197) states that, with the exception of 1-phenylbutadiene, the dimers of conjugated dienes and trienes are cyclohexenic compounds.

Allied to the dimerization reactions are those reactions in which hydrocarbons act as the dienophiles, though these hydrocarbons may not be dienes or result from the dimerization reaction type of diene synthesis. Styrene is such a hydrocarbon, as is its relative, indene. Certain other hydrocarbons have been discussed in connection with the reactions of certain dienes, such as the cyclones, myrcene, alloöcimene, etc. Hydrogenated diphenyls may be synthesized from styrene, while indene gives rise to fluorene derivatives. Thus, butadiene and styrene give 1,2,3,6-tetrahydrobiphenyl; 2,3-dimethylbutadiene and styrene give 1,2,3,6-tetrahydro-4,5-dimethylbiphenyl; butadiene and indene give 1,1a,4,4a-tetrahydrofluorene; 2,3-dimethylbutadiene and indene give 1,1a-4,4a-tetrahydro-2,3-dimethylfluorene (17). Cyclopentadiene and indene give 1,1a,4,4a-tetrahydro-1,1-endomethylenefluorene, while cyclopentadiene and styrene give 1,2,3,6-tetrahydro-3,6-endomethylenebiphenyl (17). Inasmuch as these additions are carried out at elevated temperatures and the adduct of cyclopentadiene and styrene contains the bicycloheptene ring, there is also found a quantity of a secondary product formed by the addition of cyclopentadiene to the active double bond of the cyclopentadiene-styrene adduct.

An isomer of the product obtained from styrene and butadiene may be obtained by decarboxylation of the adducts of 1-phenylbutadiene and acrylic or maleic acid (17). By choice of suitably substituted phenylbutadienes, butadienes, or styrenes, almost any desired hydrogenated diphenyl may be prepared. If styrene is substituted in the side chain with an aldehyde group (cinnamaldehyde), the reaction with butadiene occurs at ordinary temperatures (17):
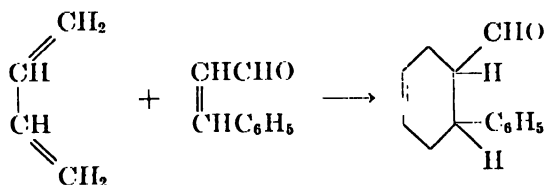

1-Phenylbutadiene and styrene should yield terphenyl derivatives:
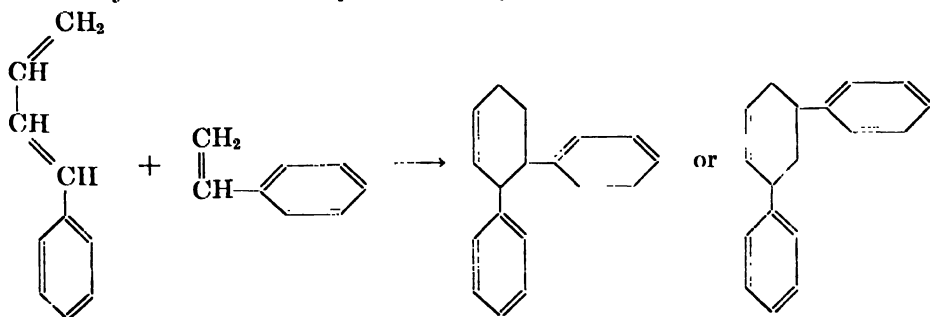
X. DIENIC ACIDS AND DERIVATIVES

Dienic acids the double bonds of which are conjugated may act as dienes in the diene synthesis. Esters of these acids can also react, as well as lactones and lactams of hydroxy- and amino-dienic acids. A fine example of the reaction of an enol as a dienic lactone is shown by γ-methylpyrone in its addition of dienophiles.

The glycerides of β-eleostearic acid and licanic acid have been shown to add maleic anhydride (258, 259). The reaction of β-eleostearic acid itself (θ,κ,μ-octadecatrienoic acid) has been reported (257) to give a product to which structure I has been assigned, although no evidence appears to have been advanced to disprove the alternative structure (II). Methyl β-eleostearate and α-eleostearic acid (295) have been shown to add maleic anhydride, and 9,11-licanic acid gives III with maleic anhydride (94).
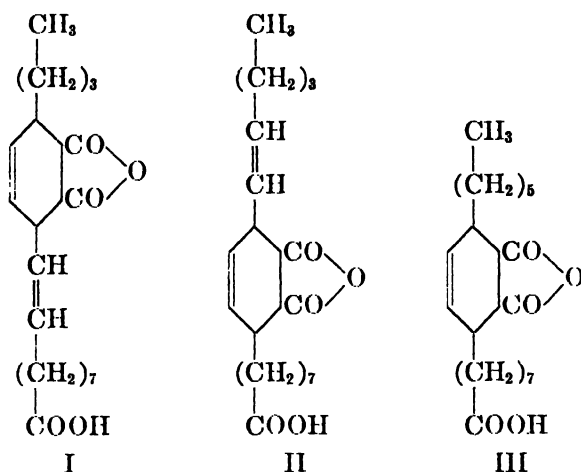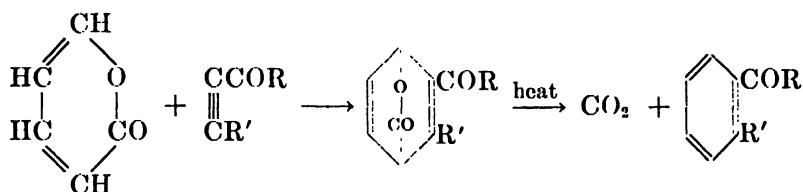

Sorbic acid forms one or more dimers (197, 272), as indicated on page 436. Kuhn and Deutsch state that only one dimer is formed (XI, page 435), basing this claim on the products obtained on decarboxylation of the dimer. Decarboxylation results in a cyclohexene which apparently undergoes isomerization to an o-propyltetrahydrotoluene. As is well known, cyclohexadiene is thermodynamically unstable, and o-propyltetrahydrotoluene appears to undergo dismutation under the pyrolytic conditions of the decarboxylation, so that the final products isolated are o-propyltoluene and o-propylmethylcyclohexane. A similar effect (272) is noted in the decarboxylations of the dimers of vinylacrylic acid and of β-styrylacrylic acid. Thus, vinylacrylic acid dimer gives trimeric hydrocarbons, ethylbenzene, and ethylcyclohexane. β-Styrylacrylic acid dimer gives biphenyls which are hydrogenated to varying extents and also biphenyl itself.

Sorbic acid esters add dienophiles. Ethyl sorbate adds benzoylethylene (47) to give 1,2,5,6-tetrahydro-3-methylbenzophenone-6-carboxylic ester, the struc-
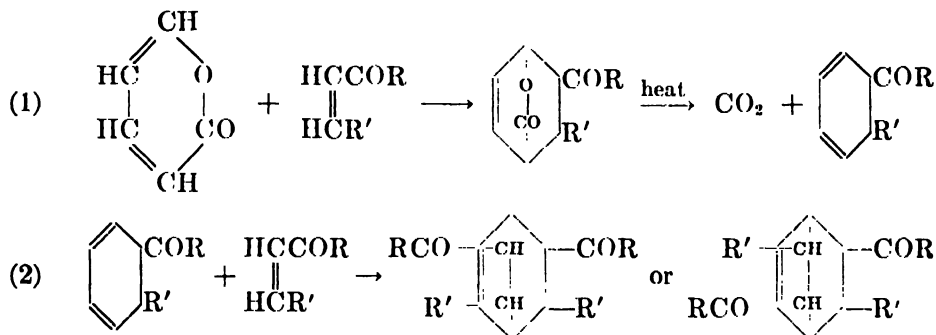
ture of which was proved. β-Chloroethyl sorbate adds acryloyl chloride (347) to give 1,2,3,4-tetrahydro-4-methylisophthaloyl dichloride, the ester group being changed into the —COCl group through the action of excess acryloyl chloride. β-Chloroethyl acrylate is the by-product.

The addition of dienophiles to the dienic lactones which contain a six-membered lactone ring engenders products containing a lactone bridge. These split out carbon dioxide on heating, and this action occurs occasionally under the conditions of the reaction. The general statement of the action will depend upon whether an acetylenic or an olefinic dienophile is employed in the reaction. Schematically, the two routes are as shown below:

(A) With an acetylenic dienophile:

$$
\begin{array}{c}
\text{CH} \\
\text{HC} \quad \text{O} \\
\text{HC} \quad \text{CO} \\
\text{CH}
\end{array}
+
\begin{array}{c}
\text{CCOR} \\
\text{CR}'
\end{array}
\longrightarrow
\begin{array}{c}
\text{O} \quad \text{COR} \\
\text{CO} \quad \text{R}'
\end{array}
\xrightarrow{\text{heat}}
\text{CO}_2 +
\begin{array}{c}
\text{COR} \\
\text{R}'
\end{array}
$$

(B) With an olefinic dienophile:

(1)
$$
\begin{array}{c}
\text{CH} \\
\text{HC} \quad \text{O} \\
\text{HC} \quad \text{CO} \\
\text{CH}
\end{array}
+
\begin{array}{c}
\text{HCCOR} \\
\text{HCR}'
\end{array}
\longrightarrow
\begin{array}{c}
\text{O} \quad \text{COR} \\
\text{CO} \quad \text{R}'
\end{array}
\xrightarrow{\text{heat}}
\text{CO}_2 +
\begin{array}{c}
\text{COR} \\
\text{R}'
\end{array}
$$

(2)
$$
\begin{array}{c}
\text{COR} \\
\text{R}'
\end{array}
+
\begin{array}{c}
\text{HCCOR} \\
\text{HCR}'
\end{array}
\rightarrow
\begin{array}{c}
\text{RCO} - \text{CH} - \text{COR} \\
\text{R}' - \text{CH} - \text{R}'
\end{array}
\text{ or }
\begin{array}{c}
\text{R}' - \text{CH} - \text{COR} \\
\text{RCO} - \text{CH} - \text{R}'
\end{array}
$$

If the low-temperature adduct of cumalinic ester with maleic anhydride is esterified with methanol, carbon dioxide is eliminated. The product is not a trimellitic acid derivative but a trimesic ester. Apparently atmospheric oxidation occurs during the esterification reaction (145), for oxidation of the same adduct with bromine gives trimesic acid directly.

The structures of l-pimaric acid and of abietic acid are open to question only as far as the double-bond arrangement is concerned. Various structures have been proposed for these two acids, for their maleic anhydride adducts are identical, and one acid may be transformed into the other through the agency of heat. l-Pimaric acid adds maleic anhydride readily, even at room temperature (69, 205, 316, 317, 324, 359), while temperatures of not less than 100°C. are necessary to effect addition to abietic acid. Absorption-spectra studies indicate that the double bonds of l-pimaric acid are located in a single ring of the molecule (205), a fact which is consistent with the ease of addition of maleic

anhydride. The higher temperature is evidently necessary with abietic acid so that rearrangement to *l*-pimaric acid may occur. Fieser (205) feels that such interconversion is best expressed by assignment of structure IV to abietic acid. By a simple shift of a double bond (wandering of a semicyclic double bond), abietic acid could be converted into *l*-pimaric acid, to which Fieser assigns structure V:

IV

V

VI

VII
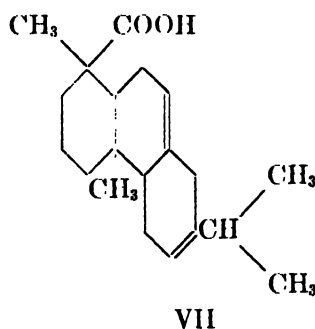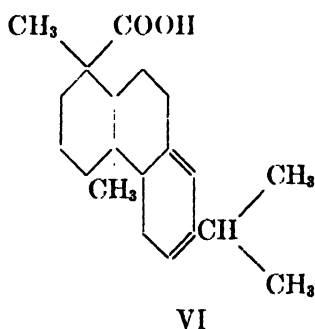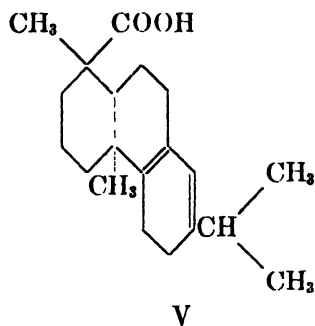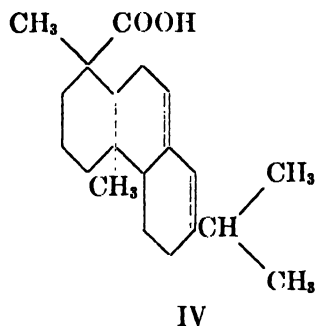
If *l*-pimaric acid has structure V, then its adduct with acetylenedicarboxylic ester should evolve ethylene on strong heating (*cf.* the section on cyclohexadiene). Sandermann (324) found that such was not the case. No olefinic gases were evolved on heating the adduct, even to charring temperatures. For this reason Sandermann prefers structure VI for *l*-pimaric acid, and has worked out a mechanism for the isomerization of abietic acid of structure IV to *l*-pimaric acid of structure VI.

It should be pointed out that, if the Fieser formulas are followed, then addition of maleic anhydride to abietic acid should be similar to the addition of maleic anhydride to β-phellandrene. β-Phellandrene (228) gives a resinous product on refluxing with maleic anhydride. When distilled *in vacuo*, this resin affords a yield of 8 per cent of the adduct of α-phellandrene and maleic anhydride. Certainly the yields of adduct from abietic acid and maleic anhydride are far higher than this, for resinous polyesters of glycerol with the abietic acid-maleic anhydride adduct are in commercial use today (304). The author feels that, in lieu of other evidence, the assumption of the existence of a conjugated

system in abietic acid is not necessary, and that it may be represented by formula VII. This is analogous to the formula of terpinolene, which is easily converted into α-terpinene (1,3-*p*-menthadiene) by a variety of agents. A semicyclic double bond such as is given in formula VII tends to wander into the more unsaturated ring, and if abietic acid be formulated as VII, it would seem reasonable to expect wandering of the semicyclic double bond to give *l*-pimaric acid, as represented by formula VI. Repeated crystallization of abietic acid from methanol will bring about the change into *l*-pimaric acid, as will also heat.

    d-Pimaric acid differs from *l*-pimaric acid in not adding maleic anhydride (359), *p*-benzoquinone, or α-naphthoquinone. These are added readily by *l*-pimaric acid at room temperature, and by abietic acid at higher temperatures (359). *p*-Xyloquinone is not added by any of these acids.

### XI. AROMATIC POLYNUCLEAR HYDROCARBONS AND CERTAIN DERIVATIVES AS DIENES

Benzene, the simplest of the aromatic hydrocarbons, does not react with maleic anhydride or with indene (291). An adduct, hypothetically obtainable from benzoic acid and maleic anhydride, probably could be obtained by addition of propiolic acid to 1,2-dihydro-*o*-phthalic acid:
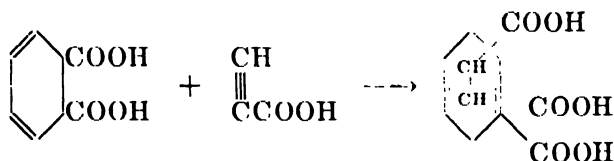
In like manner, biphenyl (61) is inert toward *p*-benzoquinone, and naphthalene (291) is inert toward indene and *p*-benzoquinone. As a general rule, those polynuclear aromatic hydrocarbons which add dienophiles are those for which complete Kekulé structures for all benzene rings cannot be drawn. Such hydrocarbons are anthracene, naphthacene, 1,2-benzanthracene, etc. Hydrocarbons for which complete Kekulé structures can be drawn, such as benzene, naphthalene, and phenanthrene, almost invariably do not add dienophiles. Chrysene appears to be an exception to this rule, and 9,10-anthraquinone may be another exception.

    Oddy (299), in 1923, observed a reaction between anthracene, maleic anhydride, and aluminum chloride and thought the product to be 9-anthroylacrylic acid. Research by the I. G. Farbenindustrie Aktiengesellschaft led to the issuance, in 1927, of a patent (239) covering the additions of α- and β-chloropropionic acids (which form acrylic acid *in situ*), acrylic, maleic, cinnamic, and crotonic acids, their esters, halides, and anhydrides to anthracene, 1,2-benzanthracene, chrysene, and their alkyl, alkoxyl, hydroxyl, and halogen derivatives to yield carboxylic acids or their derivatives suitable for use as dye or pharmaceutical intermediates. This patent appears to have been overlooked by Clar and by

Diels and Alder, for as late as 1930 Clar and John (119) were of the opinion that the reaction product of p-benzoquinone and pentacene was of structure I:

I
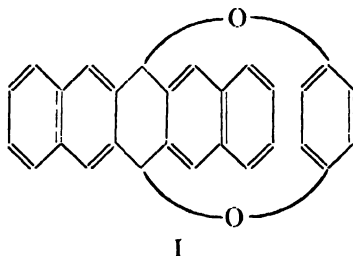
In 1931 Clar arrived at the true structure of the adduct (107) and investigated the reaction of anthracene with p-benzoquinone. Diels and Alder (138) immediately classified these reactions as diene syntheses and investigated the reactions of anthracene with other dienophiles. With maleic anhydride there was obtained an adduct of the same melting point as Oddy's compound.

The general statement of the anthracene–dienophile reaction is

$$
\text{anthracene} + \begin{matrix} CR_2 \\ \| \\ CR_2 \end{matrix} \longrightarrow \text{(adduct with } CR_2\text{–}CR_2 \text{ bridge)} \quad \text{which may be written as} \quad \text{(adduct with } R_2\text{...}R_2)
$$

Reversal of this reaction is to be anticipated, since the adducts possess the same type of ring structure as do adducts of 1,3-cyclohexadiene and acetylenic dienophiles (II).

II
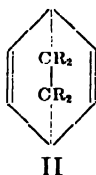
It will be recalled that the —CR_2—CR_2— bridge splits out when the adducts of cyclohexadienes with acetylenic dienophiles are heated, to yield an olefin, CR_2=CR_2. These adducts may, in a sense, be regarded as the adducts of the benzene derivative and the olefin, although such generators do not react in the diene synthesis to any measurable extent.

The extent of the reversal of the anthracene–dienophile reaction is dependent on the dienophile used; this is also true of other polynuclear hydrocarbons. In the case of anthracene adducts it has been shown that reversal is also dependent on substituents in the diene and their location on the three rings. Electronegative substituents and alkyl radicals have little or no effect when attached to positions in the terminal rings, but such substituents on the meso-positions may seriously decrease the tendency for adduct formation. This tendency reaches a maximum when the 9-substituent is the hydroxyl group, for adducts of the enol-form of anthrone appear incapable of existence (72). While anthrone will react with maleic anhydride, the reaction is not a diene synthesis (72). Hydrolysis of certain 9-substituted anthracene adducts of maleic anhydride,

such as those derived from 9-chloro- or 9-acetoxy-anthracene, would ordinarily be expected to lead to an adduct of the enol-form of anthrone with maleic anhydride. Instead, maleic anhydride (or acid) and anthrone are formed (72).

When the 9,10-substituents are alkyl groups, little effect is produced with regard to the end result of the synthesis. Usually the reaction rate is increased and the equilibrium point is nearly that of the parent hydrocarbon. Thus, 9,10-dimethylanthracene reacts much more rapidly than anthracene. 9,10-Diethylanthracene reacts more slowly, but still is more reactive than the parent hydrocarbon (391). 9,10-Diarylanthracenes react more slowly and incompletely than anthracene itself.

Linear fusion of benzene rings to the anthracene molecule favors addition of dienophiles, whereas angular fusion of the same rings tends to hinder such addition. Cook (125) took advantage of this phenomenon to separate 1,2-benznaphthacene from the 1,2,5,6- and 1,2,7,8-dibenzanthracenes, for the more nearly linear compound reacts much more readily with maleic anhydride than do the angular dibenzanthracenes.

As a typical diene, anthracene adds even such dienophiles as azodicarboxylic ester (170), giving III, and indene (291) to give IV:

III   IV   V
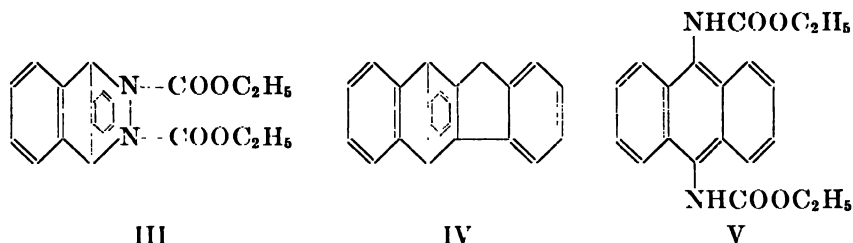
Oxidation of adduct IV gives 9,10-anthraquinone, thus indicating the points of addition. Heat decomposes adduct III into its generators, and the N—N bond of III is catalytically broken by hydrogen ion to give what is thought to be 9,10-bis(carboxyamino)anthracene diethyl ester (V).

The maleic anhydride adduct of anthracene, VI, is also oxidizable to anthraquinone, as are the anthracene adducts of dibromomaleic anhydride, citraconic anhydride, and crotonic acid (149) and also the anthracene adduct of acrylic acid (73). The adduct of dibromomaleic anhydride (VII) may be debrominated by platinum and hydrogen to give the adduct obtainable directly from anthracene and acetylenedicarboxylic acid. Acrolein adds to anthracene (335) to give VIII, but incorporation of sulfurous acid into the reaction mixture stabilizes the acrolein to such an extent that a temperature of 130°C. is required for addition to take place.
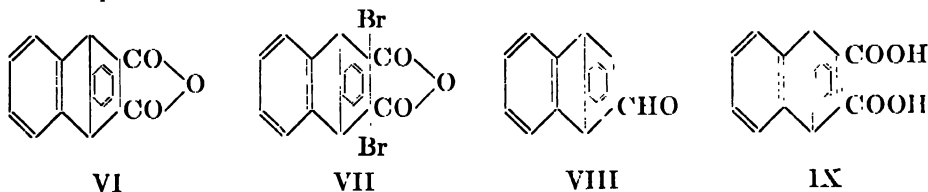

VI   VII   VIII   IX

TABLE 8

TABLE 8

Addition of acetylenedicarboxylic ester to dienic acids and their derivatives

DIENE	DIENE STRUCTURE	PRODUCT STRUCTURE	REFER-ENCE
β-Chloroethyl sorbate............			(347)
Cumalin...........			(14)
Cumalinic ester.....			(14)
Isodehydracetic acid..............			(14)

TABLE 8—*Concluded*

DIENE	DIENE STRUCTURE	PRODUCT STRUCTURE	REFER-ENCE
Enol-form of γ-methylpyrone ..			(14)
l-Pimaric acid			(321)

Acetylenedicarboxylic acid adds to anthracene to give an adduct (IX) which is rather reactive as a dienophile (149, 158). This adduct dienophile adds butadiene to give X, 2,3-dimethylbutadiene gives XI, and analogous compounds are formed with 1,1,3-trimethylbutadiene, cyclopentadiene, and 9-bromoanthracene. The structure of the adduct of 9-bromoanthracene may be inferred from that of the adduct XII, which is formed by combination of a second mole of anthracene with the initial adduct.


COOH   COOH   COOH

COOH   COOH   COOH

X   XI   XII
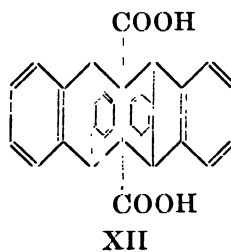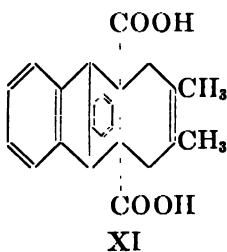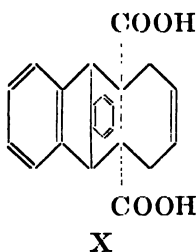
The decomposition of X on heating is of interest in that it indicates that the 1:1 anthracene–acetylenedicarboxylic acid adduct is less stable than the 1:1 butadiene–acetylenedicarboxylic acid adduct, for anthracene and 3,6-dihydrophthalic acid are obtained. However, interaction between these two products occurs, so that phthalic acid and 9,10-dihydroanthracene are also found. The higher the operating temperature, the greater is the amount of interaction. Low-temperature decomposition is best favored by operating *in vacuo* (158).

The addition of *p*-benzoquinone to anthracene yields two products. The first of them is XIII, which can add another mole of anthracene to yield the second product (XIV). Cautious oxidation of XIII yields 9,10-dihydro-9,10-endo-*o*-phenylene-1,4-anthraquinone (XV); more energetic oxidation gives 9,10-anthraquinone (107). In similar fashion, XIV may be oxidized to the corresponding tetrahydro-bis-endo-*o*-phenylenepentacenequinone.
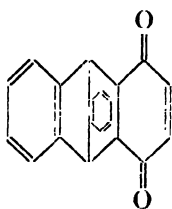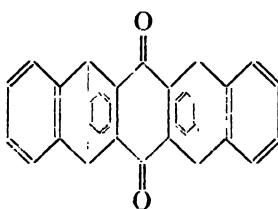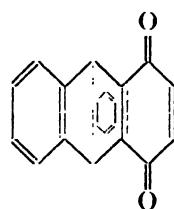
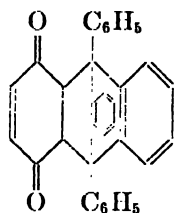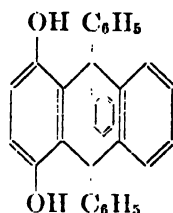XIII   XIV   XV

The adduct (XVI) of equimolar quantities of 9,10-diphenylanthracene and *p*-benzoquinone isomerizes in part to give a hydroquinone (XVII), which combines with unchanged adduct to give a quinhydrone (107).

XVI   XVII

The reversibility of adduct formation of maleic anhydride with anthracene and certain of its derivatives has been studied from a quantitative standpoint (65, 66). As a reversible reaction, adduct formation obeys the law of mass action; accordingly, an increase in the concentration of one of the generators favors adduct formation. Further, an increase of temperature promotes dissociation as well as attainment of equilibrium. Table 9 gives equilibria attained in the reactions of maleic anhydride with anthracene and related compounds when dissolved in boiling xylene (138–140°C.). The effect of increase in the concentration of one of the generators is readily apparent.

The poor yield of the cholanthrene–maleic anhydride adduct may be improved by operating at a lower temperature (in boiling benzene), but the rate of attain-

ment of equilibrium is slower than in boiling xylene.   If three mole proportions
of maleic anhydride are used with benzene as solvent, the reaction is hastened
and nearly quantitative yields of adduct are obtainable.   The excess anhydride
is easily separated from the adduct (65).

In connection with the diene reactions of the carcinogenic hydrocarbons
1,2,5,6-dibenzanthracene and 3-methylcholanthrene, the sodium salt of the
maleic anhydride adduct of 1,2,5,6-dibenzanthracene is a water-soluble carcino-
genic substance (66); and the same is probably true of the sodium salt of the
corresponding 3-methylcholanthrene adduct, which was not reported as having
been investigated in this respect.

While anthracene, its 9-phenyl, and its 9,10-diphenyl derivatives may be
photoöxidized in carbon bisulfide solution, their maleic anhydride adducts are
not photoöxidizable (188).

Other simple anthracene derivatives which add maleic anhydride are 9-bromo-
anthracene (75), 9-nitroanthracene (75), 9-carboxyaminoanthracene ethyl ester
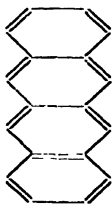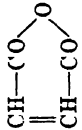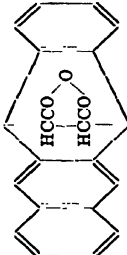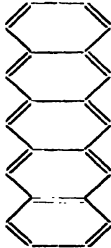
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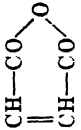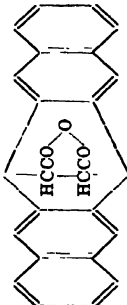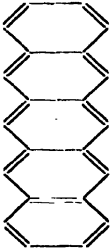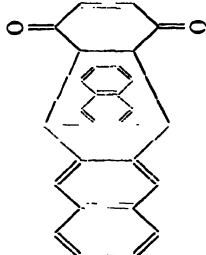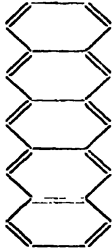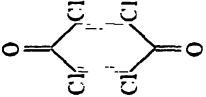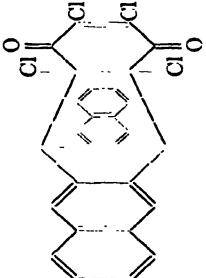
Equilibria attained in additions of maleic anhydride to anthracene derivatives in boiling xylene

DIENE	PER CENT ADDUCT WITH 1 MOLE PROPORTION OF MALEIC ANHYDRIDE	PER CENT ADDUCT WITH 30 MOLE PROPORTIONS OF MALEIC ANHYDRIDE
Anthracene	99	
9-Methylanthracene	99	
9,10-Dimethylanthracene	98	
9-Phenylanthracene	75	97
9,10-Diphenylanthracene	16	78
1,2-Benzanthracene	84	99
1,2,5,6-Dibenzanthracene	32	83
3-Methylcholanthrene	22	
Cholanthrene	15	

(75), bis-9-anthrylamine (75), and 9-bromoanthracene-10-carboxylic acid (395).
All additions occur normally in the 9- and 10-positions except for 9-amino-
anthracene.   2-Chloroanthracene and 9,10-dichloroanthracene (108) also react
normally with maleic anhydride.   The 9,10-dichloroanthracene adduct reacts
with benzene and aluminum chloride, giving 9,10-diphenylanthracene, possibly
by the formation initially of the 9,10-diphenylanthracene–maleic anhydride
adduct by the Friedel–Crafts reaction; this decomposes in part to give 9,10-
diphenylanthracene and maleic anhydride.   The last-named substance reacts
with benzene and aluminum chloride to give benzoylacrylic acid.   When
m-xylene was substituted for benzene in this reaction (108), the product was
9,10-bis(4-*m*-xylyl)anthracene.   Both arylated anthracenes were of the meso-
form, a conclusion which might have been reached on the basis of the *cis* prin-
ciple combined with the above mechanism (see the section on the stereochem-
istry of the diene synthesis, page 497).

β-Chloropropionic acid, by giving rise to acrylic acid *in situ*, reacts with

TABLE 10
Additions of dienophiles to polynuclear aromatics

HYDROCARBON	DIENOPHILE	ADDUCT	REFERENCE
	CH—CO, CH—CO (O)	HCCO HCCO	(66, 109, 386)
	CH—CO, CH—CO (O)	HCCO HCCO	(108)
	O= =O		(107)
	Cl, Cl, Cl, Cl (O, O)	O Cl Cl O / Cl Cl	(107)

(114)

(109)

(109)

TABLE 10—*Continued*
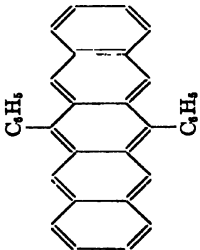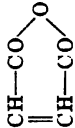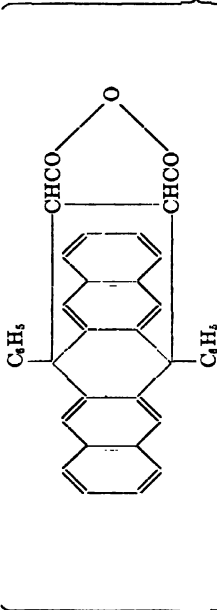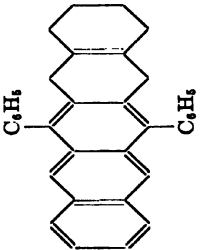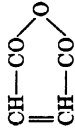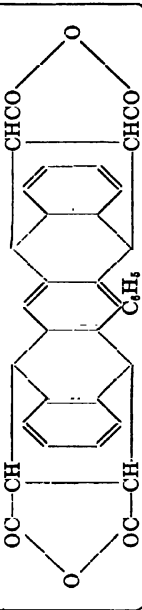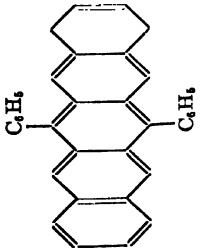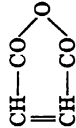
HYDROCARBON	DIENOPHILE	ADDUCT	REFERENCE
(structure with C_6H_5 ... C_6H_5)	$\begin{array}{c} CH-CO \\ \parallel \quad\quad\; \rangle O \\ CH-CO \end{array}$	(structure: C_6H_5 ... CHCO ... O ... CHCO ... C_6H_5)	(386)
		(structure: CHCO ... O ... CHCO, C_6H_5, OC—CH ... O ... OC—CH)	
(structure with C_6H_5 ... C_6H_5)	$\begin{array}{c} CH-CO \\ \parallel \quad\quad\; \rangle O \\ CH-CO \end{array}$	Adduct formed which reverts to generators on attempted isolation	(386)
(structure with C_6H_5 ... C_6H_5)	$\begin{array}{c} CH-CO \\ \parallel \quad\quad\; \rangle O \\ CH-CO \end{array}$	No reaction	(386)

(386)

(417)

(66,
109)
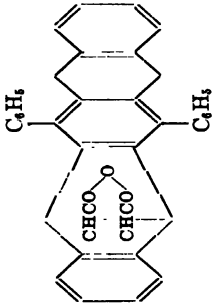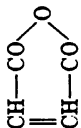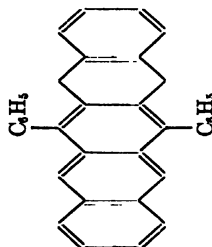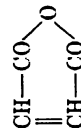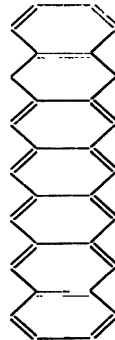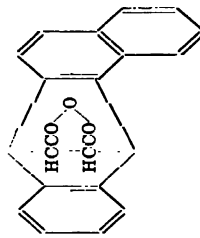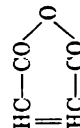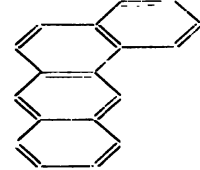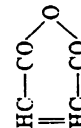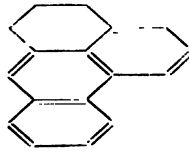
(117)

Reacts readily; product not isolated

No reaction

451

TABLE 10—*Continued*

HYDROCARBON	DIENOPHILE	ADDUCT	REFER-ENCE
			(111)
		No reaction	(110)
			(120)

(66, 124)

(116)

(108)

HCCO—O—HCCO

HC—CO
‖   ＼O
HC—CO

HC—CO
‖   ＼O
HC—CO

HC—CO
‖   ＼O
HC—CO

HCCO—O—HCCO

HCCO—O—HCCO

CH₃

CH₃

CH₃

CH₃
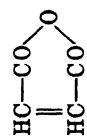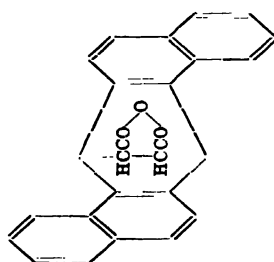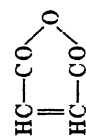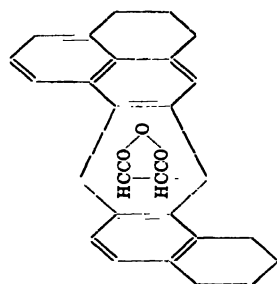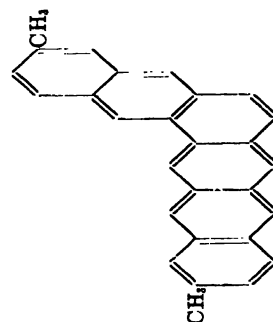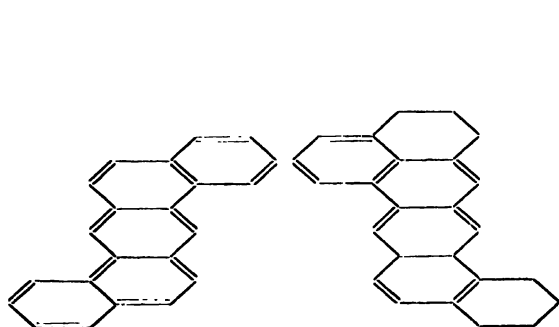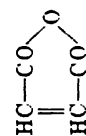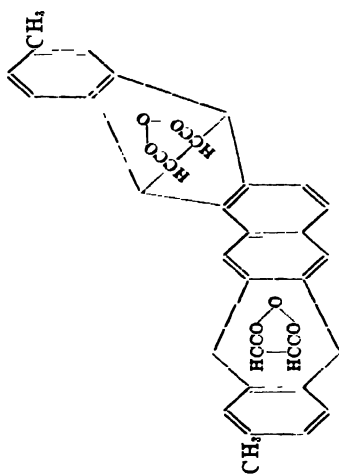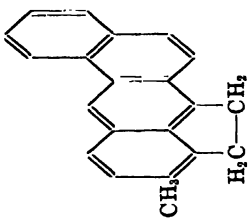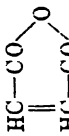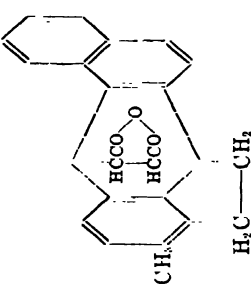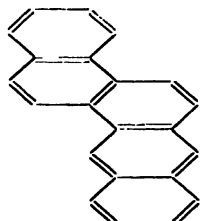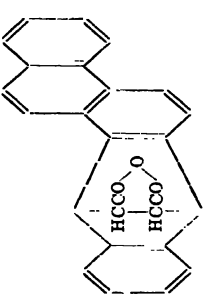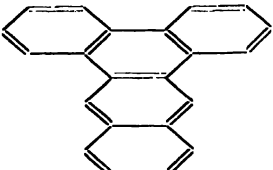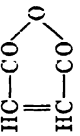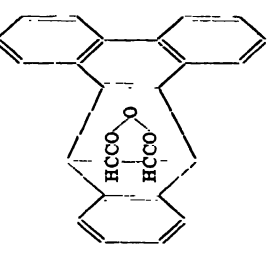
TABLE 10—*Continued*

HYDROCARBON	DIENOPHILE	ADDUCT	REFERENCE
			(66)
			(120)
			(120)
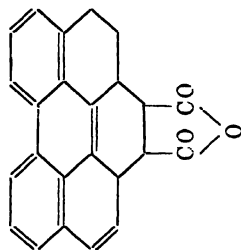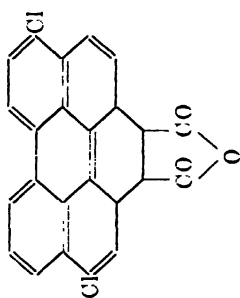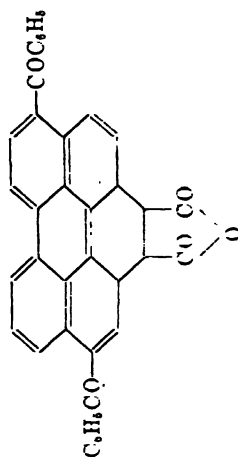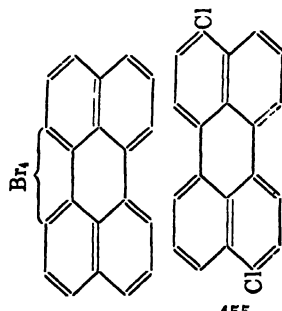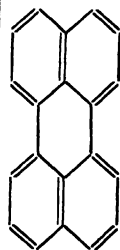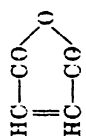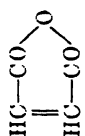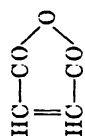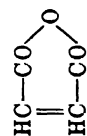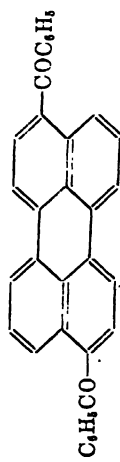
454

(110, 115)

(377)

(377)

(377)

No reaction

$HC-CO$ / O / $HC-CO$

$HC-CO$ / O / $HC-CO$

$HC-CO$ / O / $HC-CO$

$HC-CO$ / O / $HC-CO$

Cl

Cl

COC_6H_5

C_6H_5CO

CO CO O

CO CO O

CO CO O

Br$_4$

Cl

Cl

COC_6H_5

C_6H_5CO

TABLE 10—Continued

HYDROCARBON	DIENOPHILE	ADDUCT	REFERENCE
	$\underset{HC-CO}{\overset{HC-CO}{\shortmid}}\!\!>\!\!O$		(377)
	$\underset{HC-CO}{\overset{HC-CO}{\shortmid}}\!\!>\!\!O$		(110)
	$\underset{HC-CO}{\overset{HC-CO}{\shortmid}}\!\!>\!\!O$		(110)

(377)

(95)

(118)

(115)

No reaction

CO CO
O

CO CO
CH CH

CO CO
O

HC—CO
HC—CO
O

HC—CO
HC—CO
O

HC—CO
HC—CO
O

HC—CO
HC—CO
O

anthracene, 1,4-dimethylanthracene, and 9,10-dibromoanthracene as well as with 9,10-dichloroanthracene (73). With the exception of 9,10-dichloroanthracene, these compounds also add cinnamic acid.

9,10-Dibromoanthracene adds maleic anhydride at the 9- and 10-positions. The adduct is white, while the diene is yellow; hence a rough estimation of the progress of the addition may be made by noting the fading and eventual disappearance of the color. This diene does not appear to add acetylenedicarboxylic acid (149, 158).

Although anthraquinone may be considered as possessing the grouping C=C—C=O, benzene rings are fused to each of these ethylenic double bonds, and this is sufficient to prohibit anthraquinone from acting as a dienophile. However, the carbonyl groups activate the benzene rings sufficiently so that anthraquinone may act as a diene (153). This is contrary to the observations of Morrell and Samuels (295), who were unable to observe addition of maleic anhydride to 9,10-anthraquinone. According to Diels, Alder, and their collaborators, the addition of maleic anhydride to 9,10-anthraquinone (153) takes place in the 1- and 4-positions. This is shown to be the case by decarboxylation of the adduct, which yields a compound identical with that obtained by addition of α-naphthoquinone to cyclohexadiene, in which adduct the endo bridge is known to be in the 1- and 4-positions. This substance pyrolyzes to ethylene and 9,10-anthraquinone.
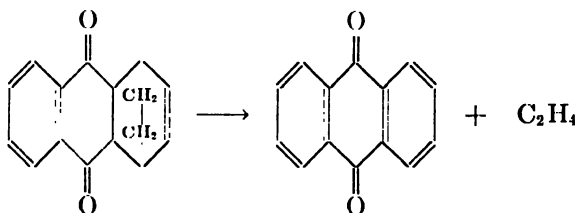
It seems likely that the benzene rings of anthraquinone are not markedly different from those of naphthalene or benzene, and this assumption leads one to the prediction that these substances will add dienophiles which are unusually reactive and the adducts of which are, in general, of high stability toward heat. For example, an adduct of benzene and maleic anhydride might be expected to decompose into its generators when heated; similarly, an adduct of benzene and acetylenedicarboxylic ester might be expected to decompose into benzene, acetylenedicarboxylic ester, phthalic acid, and acetylene.

Phenanthrene has been examined for reactivity toward dienophiles (110, 291) and, as noted previously, no additions have been observed. The existence or non-existence of such additions are of importance in connection with the old question of the distribution of the fourth valence of carbon in aromatic compounds. The most recent analysis of the evidence for and against the various proposed structures is given by Fieser (203).

Benzanthrene adds maleic anhydride (111), but the initial adduct (XVIII) undergoes rearrangement under the experimental conditions employed.

XVIII
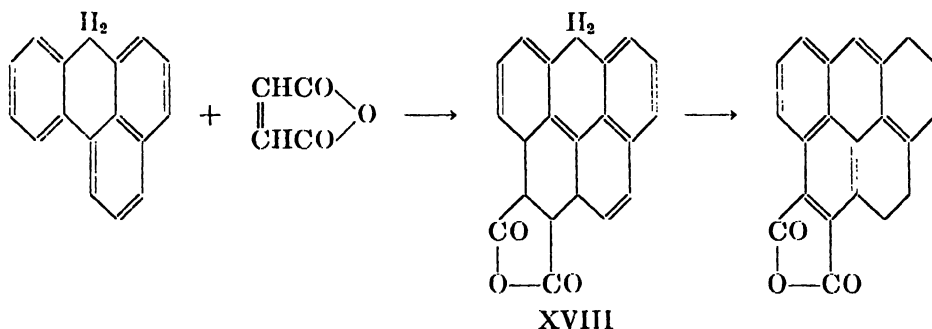
Higher polynuclear hydrocarbons in addition to those discussed above have been examined for reactivity with maleic anhydride or other dienophiles. Most of this work has been done by Clar and his collaborators, and is given in table 10.

XII. DIENE SYNTHESES BY AROMATIC HYDROCARBONS WITH UNSATURATED SIDE CHAINS

A. Vinylaromatics

The second type of polynuclear hydrocarbon to be considered is the type possessing an unsaturated side chain as substituent and acting as a diene toward dienophiles. Dienes which possess aromatic substituents will not be considered here, for they were discussed earlier. The compounds to be discussed are all homologs or benzologs of styrene and its derivatives; usually the parent aromatic hydrocarbons from which they are derived do not themselves add dienophiles, so that the mode of addition is apparent. In the addition of dienophiles by the styrene derivatives to be considered here, it is found that 1,4-addition occurs between the double bond of the unsaturated side chain and one of the Kekulé double bonds of the immediately adjacent benzene ring. A new double bond appears, which is semicyclic with respect to the former benzene ring which has now been converted into a 1,3-cyclohexadiene ring.

A tendency toward the addition of dienophiles according to the diene synthesis is possessed by styrene, which has been shown (*vide supra*) to possess dienophilic properties. Since butadiene, which usually acts as a diene, possesses dienophilic properties toward the cyclones (see cyclopentadienones) as well as toward itself, strict classification of compounds as dienes or dienophiles is sometimes difficult, and the case of styrene is one of the many examples of this problem.

One may recall that styrene polymerizes readily, and it may be that the diene synthesis plays an important part in this polymerization. Kuhn and Wagner-Jauregg (273) found that styrene adds an equimolecular quantity of maleic anhydride in boiling xylene solution. The product is polymeric; no monomeric adducts were found.

Despite the above report that no monomeric adduct is obtained from styrene and maleic anhydride, anethole (1-(*p*-methoxyphenyl)-1-propene) has been reported (289) to give an adduct with maleic anhydride which is monomeric (Hudson and Robinson (409) aver that the adduct is polymeric).

CH₃
CH
CH
+   HCCO   O   →
    HCCO
OCH₃

CH₃
CO   O
CO
OCH₃
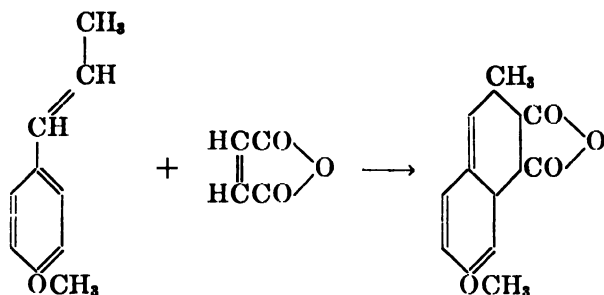
Since this adduct possesses a cyclohexadiene ring, it would be expected that a second mole of maleic anhydride could be added by the adduct. This reaction has not been reported, but in all probability will occur at higher temperatures. This expectation is realized in α-phenylstyrene (61, 346), which adds 2 moles of maleic anhydride, giving II. Presumably the compound I is formed as intermediate.

CO   O
CO

CO   O
CO
CH
CH
OC   CO
O

I   II
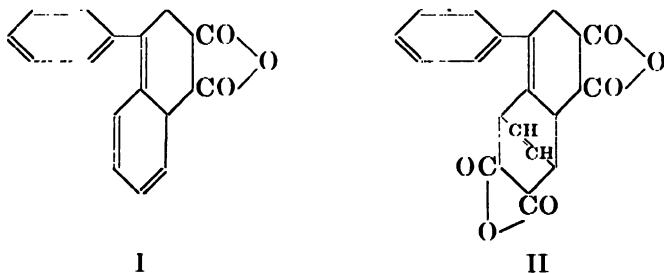
The dienophilic property of a dienophile which adds to α-phenylstyrene must be rather pronounced, for citraconic anhydride does not add (see Class A dienophiles, page 327).

Adduct II is not particularly stable, for hydrogen bromide in acetic acid simultaneously splits out maleic anhydride and rearranges the double bonds.

CO   O
CO
CH
CH₂
OC   CO
O

→   CHCO   O   +
    CHCO

CO   O
CO
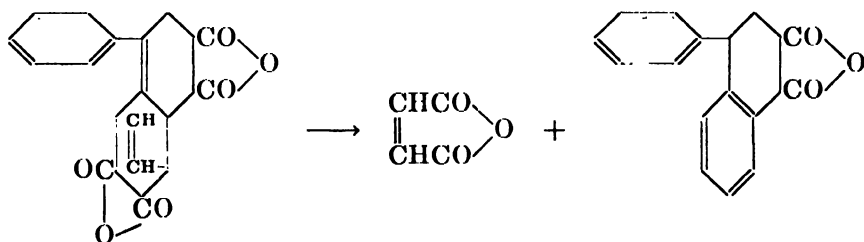
Hudson and Robinson (409) have made an extensive study of alkoxylated styrenes. Monomeric adducts are reported to form between isosafrole and maleic anhydride, diethyl maleate, and acetylenedicarboxylic ester. Isoeugenol also forms an adduct with diethyl maleate, as does its methyl ether. The ethyl ether of isoeugenol reacts normally with maleic anhydride to give 7-ethoxy-6-methoxy-3-methyl-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride, but forms polymeric materials with diethyl maleate. In this connection it is to be noted that these authors report that the products obtained result from

double-bond wandering in the originally formed adducts. Certain other alkoxy-lated styrenes have been studied by these authors, who conclude that if a styrene is to form monomeric adducts, it must be substituted by an alkyl group in the β-position and be alkoxylated in a meta-position to the side-chain vinyl group, and this position must be para to the carbon atom which becomes the ring-fusion atom of the adduct. Alkoxylation in the para-position to the vinyl group facilitates adduct formation but is not necessary.

In this connection, methylene-3,4-dioxyphenylmethylacetylene adds maleic anhydride:
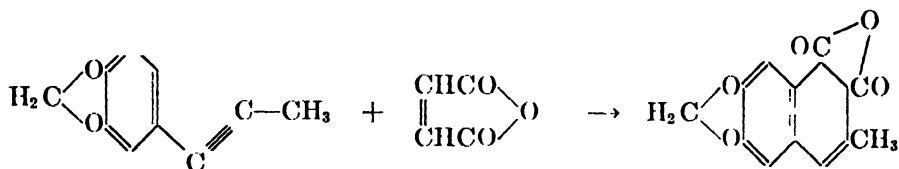
α-Vinylnaphthalene is capable of adding various dienophiles to give mono-meric adducts. Since this occurs more easily than does the styrene addition, the naphthalene nucleus therefore exhibits a lower degree of aromaticity than does the benzene nucleus. One of the standards of aromatic character is the lack of ability of the compound under observation to add dienophiles. Arbuzov (61) did not observe any condensation of maleic anhydride with α-vinyl-naphthalene, but others (67, 84, 123) were able to do so.
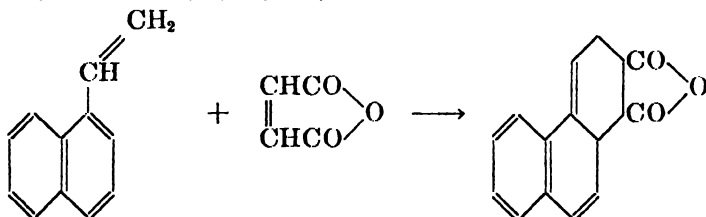
Arnold (389) reports that 5-vinyl- and 5-isopropenyl-hydrindenes polymerize in the presence of maleic anhydride. This appears to be analogous to the styrene reaction.

1-Propenylnaphthalene (206) does not add citraconic anhydride, but adds maleic anhydride to give III or IV. Fieser and Daudt are of the opinion that under the experimental conditions of this diene synthesis, wandering of a double bond of III occurs to give IV. This is not unlikely, but it has not been proved conclusively. If such is actually the case, then the adduct of 1-vinylnaphthalene and maleic anhydride has structure V instead of that given above.

III   IV   V
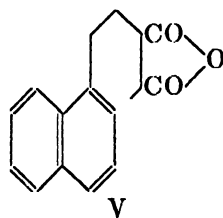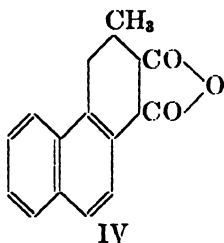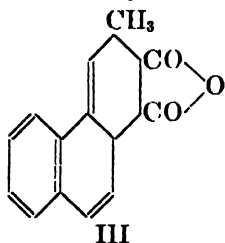
β-Vinylnaphthalene adds maleic anhydride (123) in a manner which could have been predicted from the Mills–Nixon double-bond fixation theory. The product is 2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic anhydride (VI), but double-bond migration could have occurred, so that the supposed VI is actually 1,2,3,4-tetrahydrophenanthrene-3,4-dicarboxylic anhydride (VII). Formation of 1,1a,2,3-tetrahydroanthracenedicarboxylic anhydride (VIII) would be contrary to the Mills–Nixon hypothesis, and does not occur.

VI   VII   VIII
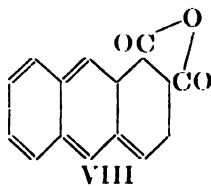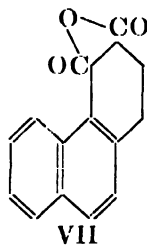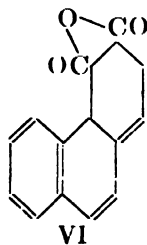
9-Vinylphenanthrene adds dienophiles to give partially hydrogenated derivatives of tri-o-phenylene. With maleic anhydride it gives IX. 9-Isopropenyl- and 9-(β-styryl)phenanthrenes form analogous products with maleic anhydride, but 9-(α-styryl)phenanthrene does not react. These styrylated phenanthrenes may be regarded as triarylated butadienes; it appears (84) to be a general rule that 1,2,3-triarylated butadienes do not add dienophiles, although the 1,1,2- and 1,2,4-isomers are capable of addition. Consequently α-(9-phenanthryl)-stilbene (87,393) does not add dienophiles.

The above examples were of simple vinylaromatics the parent aromatics of which do not add dienophiles. One case has been noted of a vinylaromatic the parent aromatic of which adds dienophiles. This is β-isopropenylanthracene (87), which could add maleic anhydride to give either X, XI, or XII. It adds but 1 mole of maleic anhydride.

IX   X

XI   XII
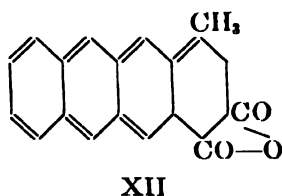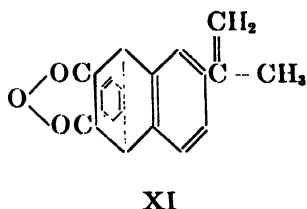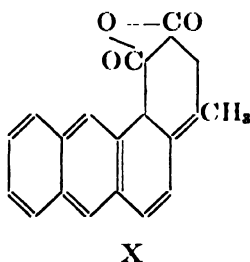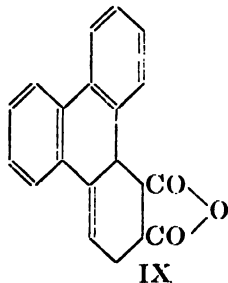
The adduct is not likely to be XII, for formation of such a product would be contrary to the Mills–Nixon hypothesis. The product is believed (87) to be XI.

Certain alicyclic derivatives of α- and β-vinylnaphthalenes have been investigated. A typical substance of this type is β-(1-cyclopentenyl)naphthalene, which adds maleic anhydride (67) to give a partially dehydrogenated sterol derivative (XIII). β-(2-Methyl-1-cyclopentenyl)naphthalene gives XIV; 6-methoxy-2-(1-cyclopentenyl)naphthalene gives XV; and α-(2-methyl-1-cyclopentenyl)naphthalene (67) gives XVI. On the other hand, α-(1-cyclohexenyl)-naphthalene (87) does not add maleic anhydride, though Bachmann and Kloetzel (67) reported the occurrence of a reaction.

XIII   XIV   XV   XVI
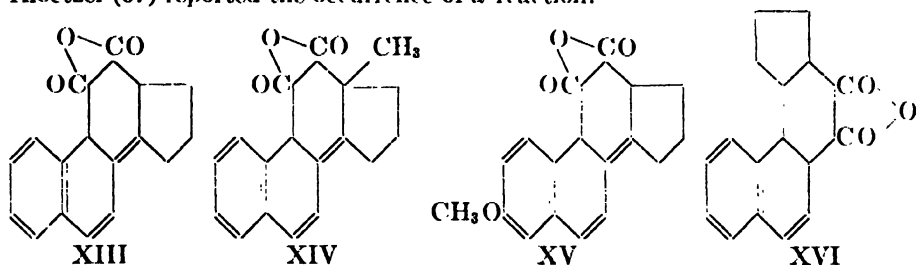
The above vinylnaphthalene derivatives which are methylated in the 2-position of the cyclenyl group add dienophiles more slowly than do their unmethylated parent compounds, for angular methyl groups appear in the adducts of the methylated vinylnaphthalene derivatives. The unmethylated cyclenylnaphthalenes add dienophiles with nearly the same ease as does vinylnaphthalene. Bachmann (67) used these compounds to synthesize the sterol-ring structure. Only one structure is possible for the final ring system when β-(1-cyclenyl)naphthalenes are used; this is an advantage not possessed by certain other syntheses of the sterol-ring system by the diene synthesis.

B. 9-Methyleneanthrone and derivatives

9-Methyleneanthrone and its derivatives add dienophiles readily to give partially hydrogenated derivatives of benzanthrones (113). In many cases these products are easily oxidized, often by atmospheric oxygen, to give benzanthrone derivatives (113). It is often found, therefore, that the products isolated from diene syntheses employing these methyleneanthrone derivatives are completely aromatic rather than hydroaromatic. It is sometimes found that 2 moles of dienophile add to the benzanthrone derivative, the second mole being regenerated when the product so obtained is oxidized to the benzanthrone derivative. This is illustrated by the reaction of methyleneanthrone with maleic anhydride (113), which proceeds in acetic acid solution according to the scheme

XVII

XVIII

XIX
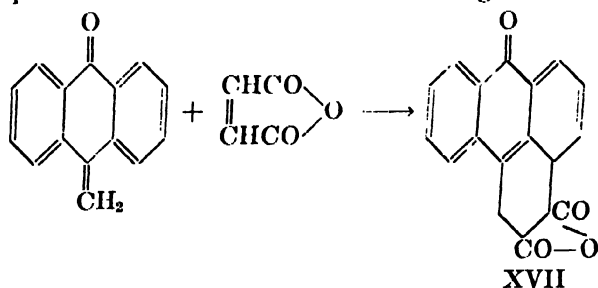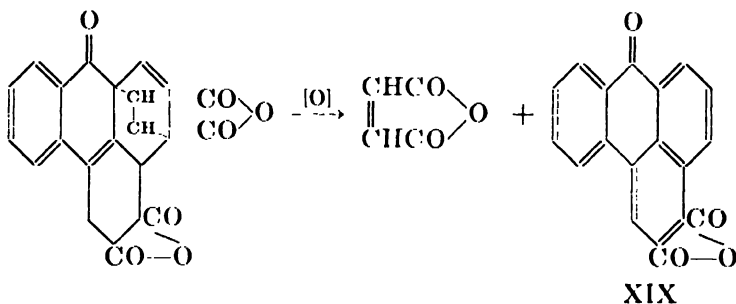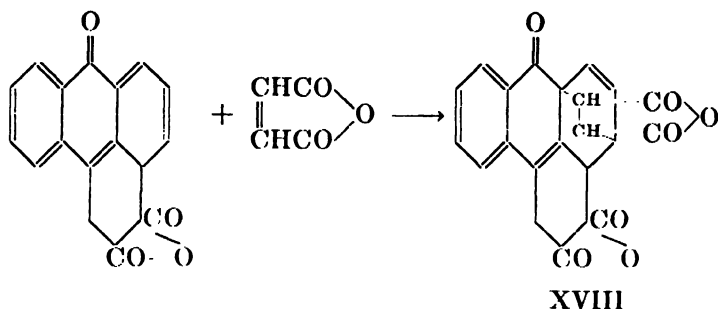
The initial adduct (XVII) contains the cyclohexadiene ring, and therefore is capable of addition of the second mole of maleic anhydride to give XVIII. Oxidation of XVIII yields maleic anhydride and XIX. If the generators are fused together in the presence of air or with an oxidizing agent or solvent (251), addition and dehydrogenation occur simultaneously; upwards of 50 per cent yields of XIX are obtained.

The I. G. Farbenindustrie A.-G. owns a patent (251) which covers the additions of the following dienophiles to methyleneanthrone: maleic anhydride, cinnamic acid, ethyl cinnamate, fumaric acid, crotonaldehyde, benzalacetophenone, stilbene, butadiene, and β-chloropropionic acid (which reacts by forming acrylic acid *in situ*). All additions are conducted in the presence of an oxidizing agent or solvent, usually nitrobenzene. As a result, the hydroaromatics originally formed are dehydrogenated, and the products isolated from the reaction mixtures are completely aromatic.

This dehydrogenating action of nitrobenzene is rather general. Bergmann (394) has obtained 3,6-diphenylphthalic anhydride by boiling 3,6-diphenyl-1,2,3,6-tetrahydrophthalic anhydride with nitrobenzene. The method has its limitations, as pointed out by Bergmann. *m*-Dinitrobenzene, *p*-chloronitrobenzene, and *p*-bromonitrobenzene exhibited no dehydrogenating effects at 140°C. or lower; apparently higher temperatures were not tried. The usual operating temperature range for nitrobenzene is 200–250°C.

Addition of cinnamic acid (113, 251) to methyleneanthrone in boiling nitrobenzene gives *Bz*-1-phenylbenzanthrone, decarboxylation occurring during the synthesis.

$$+ \quad C_6H_5CH{=}CHCOOH \quad \xrightarrow{\text{[O]}}$$

$$CO_2 \quad + \quad \qquad + \quad 2\,H_2O$$
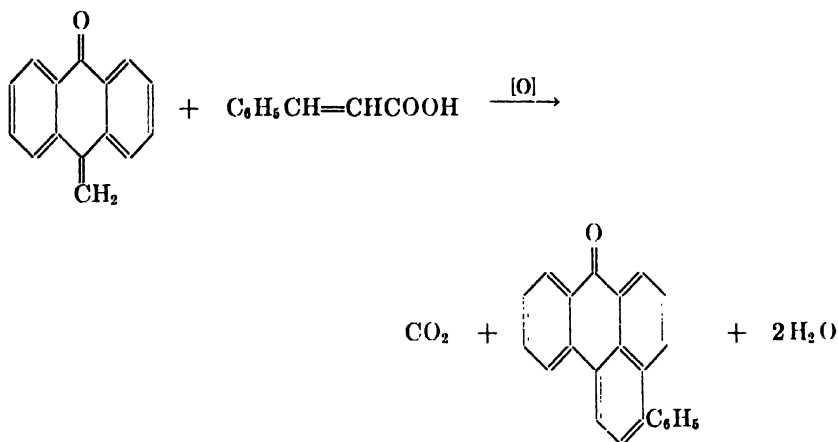
A similar decarboxylation occurs in the addition of fumaric acid, the product being XX. Benzoylethylene (47) gives what is believed to be XXI; structure XXII for the product is less likely but not impossible. Stilbene (47) gives XXIII.

XX

XXI

XXII

XXIII
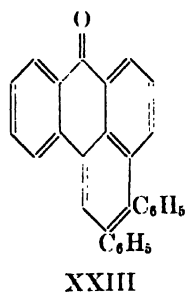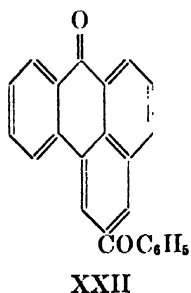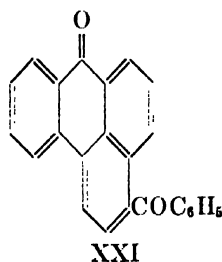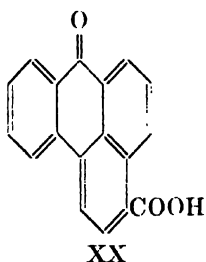
Methyleneanthrone also adds quinones. When excess methyleneanthrone reacts with p-benzoquinone (113), atmospheric oxidation of the initial product results in the formation of bis-(benzanthrono-Bz-1,2)-2.3,5,6-p-benzoquinone (XXIV). Clar appears to have overlooked the possibility of an unsymmetrical structure (XXV) for the product.
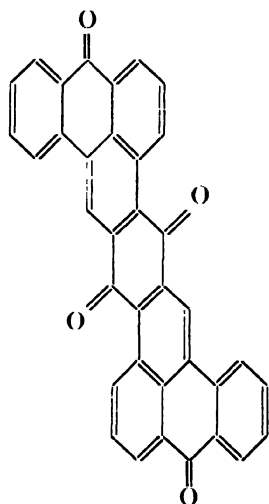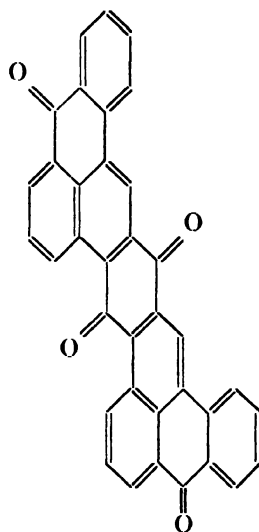
XXIV   XXV

When chloranil and methyleneanthrone react, the oxidation step is unneces-
sary, since this was accomplished during the chlorination of the quinone. Elimi-
nation of hydrogen chloride from the initial product (XXVI) gives XXVII.
Addition of excess methyleneanthrone to chloranil results in the loss of hydrogen
chloride and formation of the same product that is obtained by the oxidative
addition of methyleneanthrone to *p*-benzoquinone, XXIV or XXV.
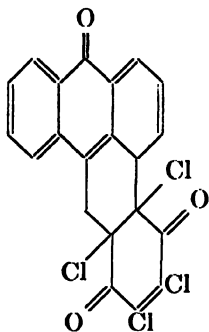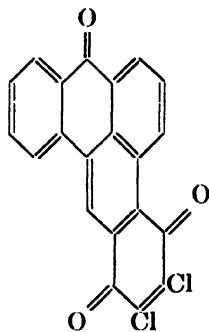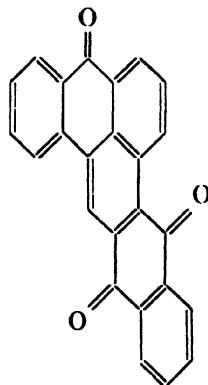
XXVI   XXVII   XXVIII

Interaction of air, methyleneanthrone, and α-naphthoquinone gives (XXVIII).
This product might also be formed by reaction of butadiene with XXVII, fol-
lowed by dehydrochlorination of the resulting product.

9,10-Dihydro-9,10-*o*-phenylene-1,4-anthraquinone (prepared by addition of
1 mole of anthracene to 1 mole of *p*-benzoquinone, followed by gentle oxidation

of the adduct) adds to methyleneanthrone in the presence of air to give XXIX as the final product. The structure of the butadiene adduct (251) with methyleneanthrone is given as XXX, although other structures such as XXXI do not appear to have been excluded from consideration. The symmetrical nature of XXX is the sole advantage of that structure.
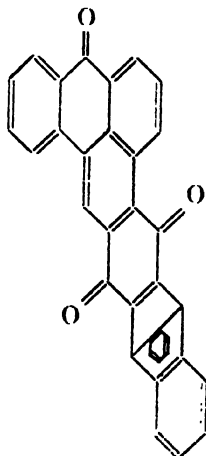
XXIX   XXX   XXXI
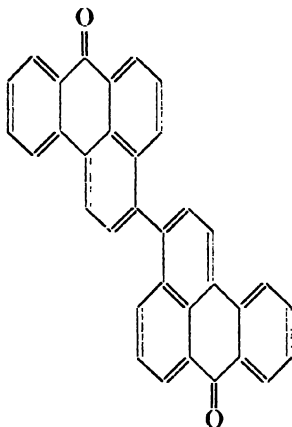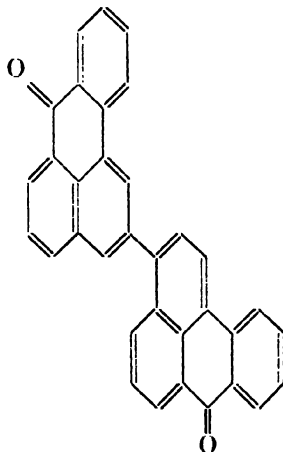
ω-Phenylmethyleneanthrone (benzylideneanthrone) adds dienophiles (112, 113); with maleic anhydride, XXXII is formed in the presence of air, while fumaric acid forms what is thought to be XXXIII, decarboxylation occurring in the Bz-1-position. It will be recalled that in the additions of fumaric and cinnamic acids to methyleneanthrone itself, decarboxylation was postulated as occurring in the Bz-2-position of the initial or oxidized adducts.

ω-(2-Anthraquinoyl)methyleneanthrone (112, 113) reacts with maleic anhydride and air to give XXXIV.
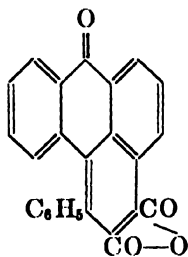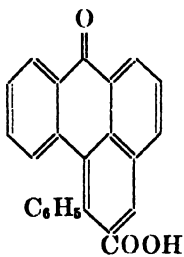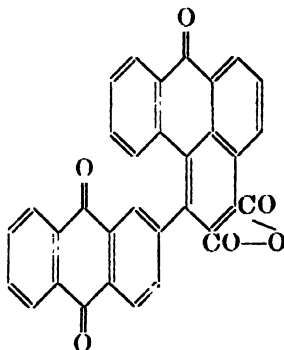
XXXII   XXXIII   XXXIV

XIII. HETEROCYCLIC DIENES

A. *Thiophene and derivatives*

Thiophene is closely related to benzene and furan. Like benzene, thiophene is stated not to add dienophiles (135), and the same probably applies to homologs such as the thiotolenes and thioxenes. Thionessal does not add dienophiles (400). Also, even though the isobenzofurans add dienophiles, the isobenzothiophenes do not (186). It is also likely that the selenophenes do not add dienophiles.

Reinvestigation of the above may result from the recent work of Clapp (400), who was able to add maleic anhydride to 2,3,4,5-bis(1,8-naphthalene)thiophene at 255°C., obtaining 3,4,5,6-bis(1,8-naphthalene)phthalic anhydride. The hypothetical addition product apparently lost hydrogen sulfide to yield the substituted phthalic anhydride:
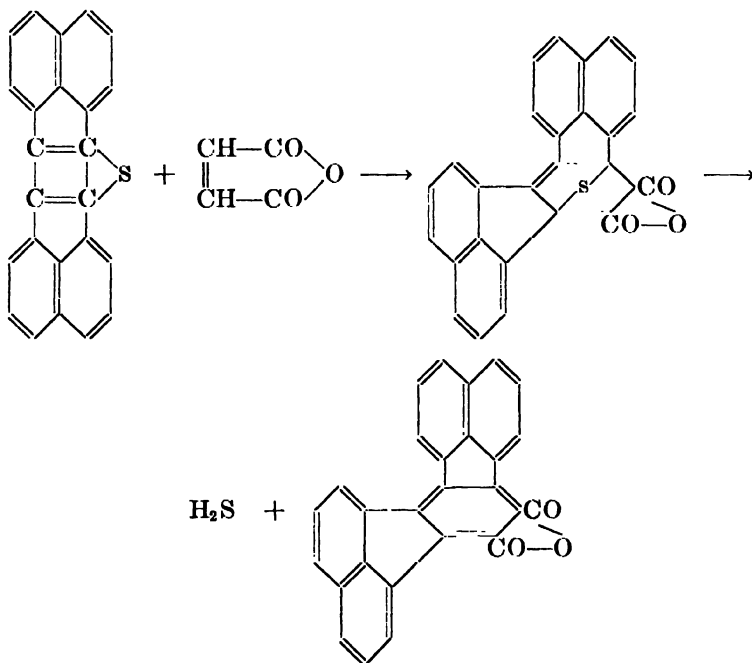
B. *Furan and derivatives*

Furan contains the conjugated-double-bond system required of dienes which undergo the diene synthesis. Indeed, the most extensively studied of the dienophiles (maleic anhydride) may be regarded as the quinone of furan (301). Like the aromatic quinones, it forms colored complexes with polynuclear aromatics, phenols, and arylamines, and responds to the triphenylphosphine test (326, 327) for quinones. Its addition of dienes resembles those of quinones; however, diene addition is by no means a property peculiar to quinones, especially since many quinones, such as anthraquinone, do not add dienes. Anthraquinone

is the lowest benzolog of p-benzoquinone possessing benzene rings fused to each of the two carbonylenic double bonds. The lowest benzolog of furanquinone is phthalic anhydride, which also does not add dienes.

Except under certain highly restricted conditions, the addition of dienophiles by furan and its derivatives results in what is termed an oxygen bridge. Thus furan and maleic anhydride react to give I, possessing the oxygen bridge.

In the study of the usual two-dimensional structural pictures of these and other bridged compounds, care must be taken to avoid the impression that a so-called bridge possesses extraordinary and unique properties. A three-dimensional model of a bridged compound shows that such an assumption is invalid and that, save for convenience in nomenclature, there is no reason for stating that one or another group of atoms forms the bridge, and that the remainder of the molecule is more like the common simple compounds. Thus the furan-maleic anhydride adduct may be represented by three structures:
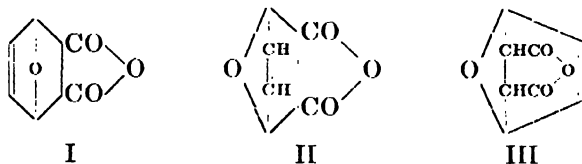
It should always be kept in mind that the bridge, as such, does not confer special properties on the atoms included in that bridge, although the natural human tendency appears to be that one will tend to place the more reactive portion of the molecule in the bridge on drawing the structure of such a bridged compound. The tendency is shown in the papers of Diels, Clar, Dane, Butz, Alder, Fieser, and many others. Oftentimes it is most convenient to place the most reactive portion of the molecule in the bridge, for it is usually smaller (from the point of view of writing the structures) than the less reactive portions of the molecule. Though the adduct of cyclohexadiene and acetylenedicarboxylic ester splits out ethylene on heating, it is no less correct to write its structure as V or VI as well as IV, which is the usual notation.
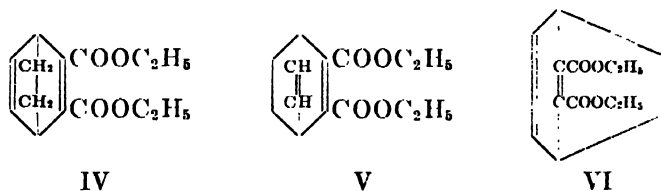
For convenience, however, the usual methods of structure designation and nomenclature of bridged compounds have been followed in this paper. Hence in discussion of adducts of furan and related compounds, reference will be made to the oxygen bridge, though it is no more of a bridge than other portions of the molecule under consideration.

The oxygen bridge is thermodynamically stable in most respects, particularly so toward heat. Heating of furan adducts almost invariably results in resolution

into their generators or else into pyrolytic decomposition products of these generators. Occasionally decomposition occurs in other portions of the molecule, but the oxygen bridge is almost never ruptured by heat alone (14, 146).

The adducts of the furans with acetylenedicarboxylic esters or the acid itself may be hydrogenated in stages (10, 166), first giving VII and eventually VIII.

$$\text{VII} \qquad \text{VIII}$$
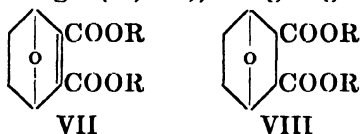
The partially hydrogenated adduct of sylvan (α-methylfuran) and acetylenedicarboxylic ester, corresponding to VII in structure, evolves ethylene on heating (14) and forms 2-methyl-3,4-furandicarboxylic ester:

$$\text{(structure)} \longrightarrow C_2H_4 + \text{(structure)}$$
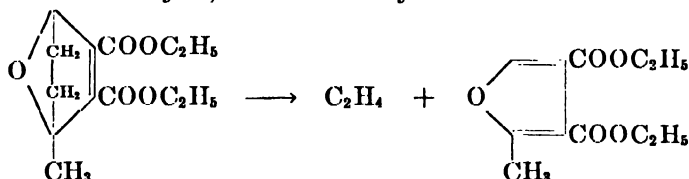
The partially or fully hydrogenated adducts of acetylenedicarboxylic ester and other acetylenic dienophiles with furans and also the hydrogenated adducts of ethylenic dienophiles with furans are attacked by hydrogen chloride or bromide to open the oxygen bridge. That this is reasonable may be seen when it is noted that such hydrogenated adducts are derivatives of tetramethylene oxide, the ring of which may be ruptured by treatment with hydrogen halides to give tetramethylene halides. When the bridge carbon atoms (those to which the oxygen bridge is attached) possess alkyl or aryl substituents, the dihalo compound which results by action of hydrogen halides usually dehydrohalogenates spontaneously to give cyclohexadiene derivatives. When no such substituents are present, the dihalo compound usually can be isolated, but only slight heating is necessary to cause dehydrohalogenation and formation of the cyclohexadiene derivative (14, 146):

$$\text{(structure)} + 2HCl \longrightarrow H_2O + \text{(structure)} \longrightarrow 2HCl + \text{(structure)}$$
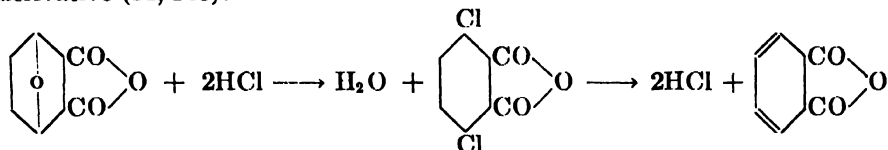
Similar treatment of the partially hydrogenated adducts of the furans with equimolar quantities of acetylenic dienophiles (14, 146) yields benzene derivatives:

$$\text{(structure)} + 2HCl \longrightarrow H_2O + \text{(structure)} \longrightarrow 2HCl + \text{(structure)}$$
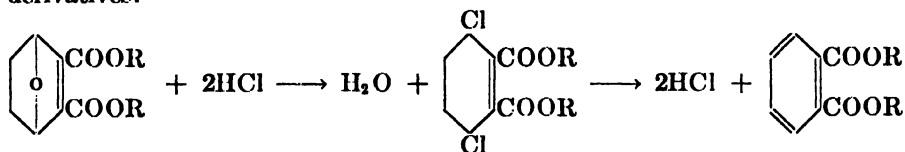
The action of hydrogen halides on the unhydrogenated adducts has not been reported, but it would most likely give a mixture of derivatives of phenol and halobenzene.

The adduct of furan and maleic anhydride will add hypobromous acid to give a compound (IX) which lactonizes easily, yielding X. This lactone acid is sensitive to hydrogen halides, for hydrogen bromide ruptures the bridge and simultaneous dehydration and dehydrohalogenation result in the formation of phthalic acid (14). In like manner, the adduct of 2 moles of furan with 1 mole of acetylenedicarboxylic acid will form a monolactone and eventually a dilactone (XI) with hypobromous acid (166).
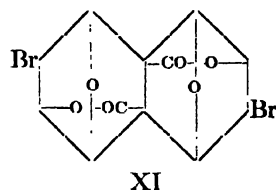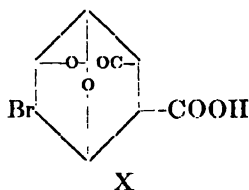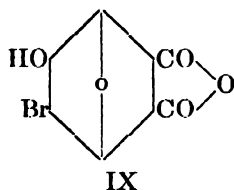
It may be seen that certain of the above reactions are adaptable to the preparation of 1,3-cyclohexadiene. The reduced adduct of furan and maleic anhydride (VIII), which is also formed by complete reduction of the adduct of equimolar quantities of furan and acetylenedicarboxylic acid, may be treated with hydrogen bromide and the resulting compound (XII) dehydrobrominated to give a cyclohexadienedicarboxylic acid (XIII or XIV). This may be decarboxylated to yield 1,3-cyclohexadiene. Oxidation of the dicarboxylic acid, which is either XIII or XIV, yields phthalic acid. Similar reaction sequences are shown by substituted furans, and the method offers means of preparing substituted
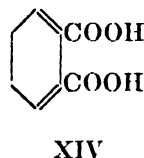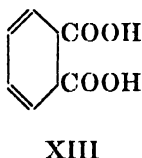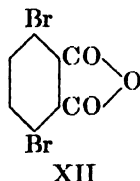
cyclohexadienes. Examination of the adducts of the substituted cyclohexadienes should offer circumstantial evidence which will permit a tentative choice between formulas XIII and XIV.

When working with the fully hydrogenated adducts of furans and maleic anhydride, one should bear in mind that these materials are vesicant (146, 148).
. The additions of furan to maleic anhydride (146, 148, 166), acetylenedicarboxylic ester (148, 166), and pyrocinchonic anhydride (135, 146) have been studied. It is of interest to note that the addition of pyrocinchonic anhydride could not be repeated (166) nor could α-methyl-β-chlorocrotonic acid (166) be added to furan. In the earlier work on pyrocinchonic anhydride additions, it was reported that cantharadin (XV) was synthesized by reduction of the double bond of the pyrocinchonic anhydride adduct.

The adduct of equimolar quantities of furan and acetylenedicarboxylic ester

will add a second and even a third mole of **furan** to give **XVI** and **XVII**, respectively (166).

XV   XVI   XVII
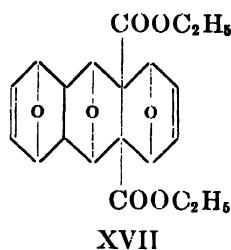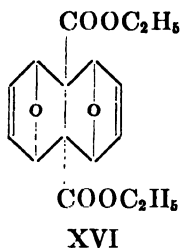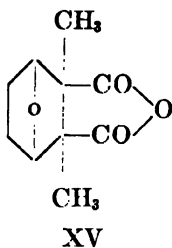
It has been found that in the presence of traces of sulfur dioxide, furan will not add acrolein according to the diene synthesis (89, 330). The reaction, which occurs only to a moderate extent, is:
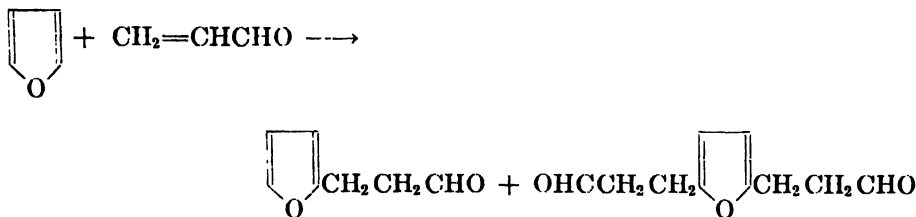
In a typical experiment, 146 g. of dry furan and 120 g. of dry acrolein were heated at 100°C. for 1 hr. with 10 mg. of sulfur dioxide dissolved in 0.5 ml. of water. Half a gram of hydroquinone had been added to stabilize the acrolein. The object of using dried materials is not known, since aqueous sulfur dioxide was used. The reaction product was 17 g. of the monoaldehyde and 30.5 g. of the dialdehyde. The reaction does not occur in the absence of sulfur dioxide or in the presence of other acidic compounds. Thus, acrylic acid gives poly-acrylic acid and unchanged furan under these conditions. Further, sulfur dioxide does not catalyze the combination of some other olefinic aldehydes with furan in this manner.

It will be shown later that this reaction of furan with acrolein is similar in type to certain reactions of pyrroles with dienophiles.

Sylvan (2-methylfuran) reacts with acetylenedicarboxylic esters and maleic anhydride and esters in the same way as does furan (9, 308). Hydrogenation of the acetylenedicarboxylic ester adducts of both furan and sylvan, using palladium and hydrogen, results in the initial reduction of one double bond so as to give 3,4,5,6-tetrahydro-3,6-endo-oxo-phthalic anhydride. It will be noted that the active double bond of these adducts is located in a position analogous to that of the cyclopentadiene–acetylenedicarboxylic ester adduct. The furan– or sylvan–acetylenedicarboxylic ester adducts are, when partially reduced, isomeric with the corresponding unreduced adducts with maleic (or fumaric) ester:

$$
\text{[furan]} \ O +
\begin{array}{l}
\text{CCOOC}_2\text{H}_5 \\
\| \\
\text{CCOOC}_2\text{H}_5
\end{array}
\longrightarrow
\text{[adduct]} \ O
\begin{array}{l}
\text{COOC}_2\text{H}_5 \\
\text{COOC}_2\text{H}_5
\end{array}
\xrightarrow{\text{[H]}}
\text{[adduct]} \ O
\begin{array}{l}
\text{COOC}_2\text{H}_5 \\
\text{COOC}_2\text{H}_5
\end{array}
$$

$$
\text{[furan]} \ O +
\begin{array}{l}
\text{HCCOOC}_2\text{H}_5 \\
\| \\
\text{HCCOOC}_2\text{H}_5
\end{array}
\longrightarrow
\text{[adduct]} \ O
\begin{array}{l}
\text{COOC}_2\text{H}_5 \\
\text{COOC}_2\text{H}_5
\end{array}
$$
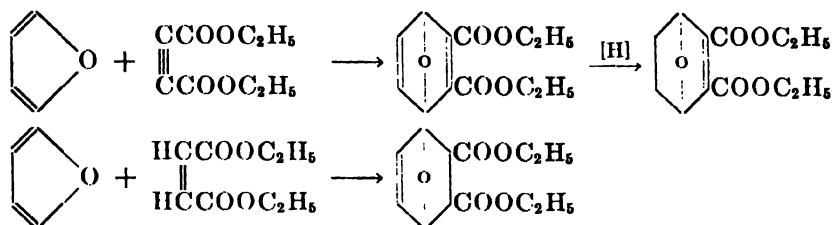
The partially hydrogenated adducts of acetylenedicarboxylic esters with furan or sylvan contain the grouping C=C—C=O; like the unhydrogenated adducts, they are able to add dienophiles. The dienophilic property is present to much the same degree as in allyl chloride (page 333), since addition of butadiene to these compounds requires a temperature of the order of 170°C. Dehydration occurs simultaneously when the original acetylenic dienophile is acetylene-dicarboxylic acid, so that the product is an anhydride of an acid containing angular carboxyl groups. When sylvan is added to the partially reduced adduct of equimolecular quantities of sylvan and acetylenedicarboxylic acid (9), the product is XVIII or the isomer with opposed methyl groups.

3-Methylfuran (308) has been observed to add maleic anhydride to give XIX. 2,5-Dimethylfuran adds maleic anhydride to give XX. The reduced adduct from XX is attacked by hydrobromic acid to give 3,6-dimethyl-1,2-dihydro-

XVIII   XIX   XX
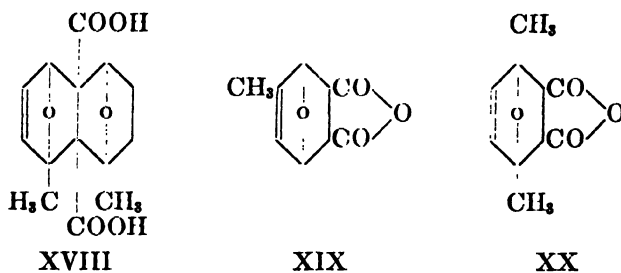
phthalic acid. The intermediate dihalo compound could not be isolated under the conditions of the experiment (146). Decarboxylation of the dimethyldi-hydrophthalic acid yields 1,4-dimethyl-1,3-cyclohexadiene. The formation of these compounds may give a clue as to the formula of the dihydrophthalic acid obtained by the action of hydrobromic acid on the reduced adduct of furan and maleic anhydride. It would appear that the dihydrophthalic acid is XIII rather than XIV. The dimethyldihydrophthalic acid may be oxidized by nitric acid to give 3,6-dimethylphthalic acid (146).

2,5-Dimethylfuran reacts with acetylene in a manner similar to certain pyrrole reactions to give acetonylideneacetone.

2-Methyl-5-isopropylfuran (97) has been observed to react with maleic anhydride. The reaction has been employed for the synthesis of cineole.

Furyl acetate is also capable of addition of dienophiles (147). The addition of maleic anhydride yields 3-acetoxymethyl-3,6-endo-oxo-1,2,3,6-tetrahydro-phthalic anhydride.

2-(β-Phenylethyl)furan adds maleic anhydride (373) to give an adduct which dissociates in solution with great ease, and must be purified by crystallization at low temperatures. When the above adduct is heated on a steam bath in a current of nitrogen, dissociation takes place to such an extent that 2-(β-phenylethyl)furan sublimes. Similar properties are shown (373) by the maleic anhydride adduct of 2-β-(m-methoxyphenyl)ethylfuran.

2-(2-Tetrahydrofurfuryl)furan (271) has been observed to add maleic anhydride. Benzoylethylene (47) does not appear to add to furan, sylvan, or 2,5-dimethylfuran.

C. Isobenzofurans

The isobenzofurans are conveniently prepared (3,6) by a diene synthesis. A symmetrical diaroylethylene is added to a simple diene to give an adduct which is then dehydrated and rearranged into a substituted dihydroisobenzofuran. The complete picture of the reactions involved is as follows:
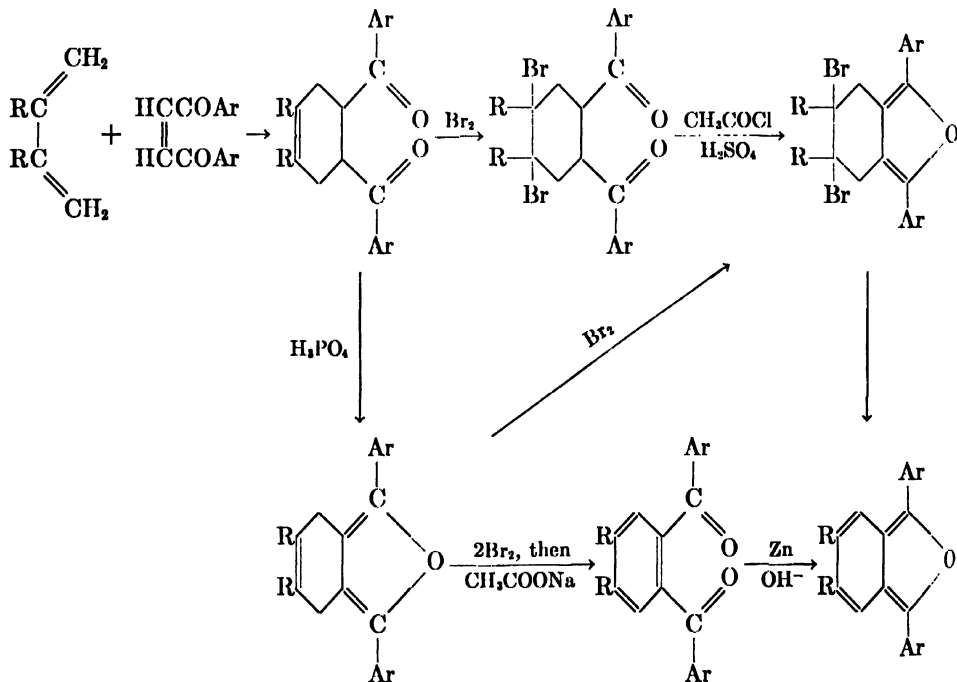
In this series of reactions, R is either hydrogen or methyl, while Ar may be phenyl, p-chlorophenyl, p-tolyl, 2-mesitylenyl, α-naphthyl, p-xenyl, or 3,5-dibromo-4-hydroxyphenyl (3, 4, 6, 355, 356). A portion of this series has been conducted using cyclopentadiene (3). 2,3-Dimethylbutadiene did not react when Ar was 2-mesitylenyl (6).

The resulting isobenzofurans will add various dienophiles. The outstanding

characteristic of the resulting adducts is their ease of dissociation into their generators, which will be illustrated later with specific examples. The adducts are, however, of great synthetic value. Dufraisse and Priou (187) prepared 1,4-diphenylnaphthalene by the following series of reactions:
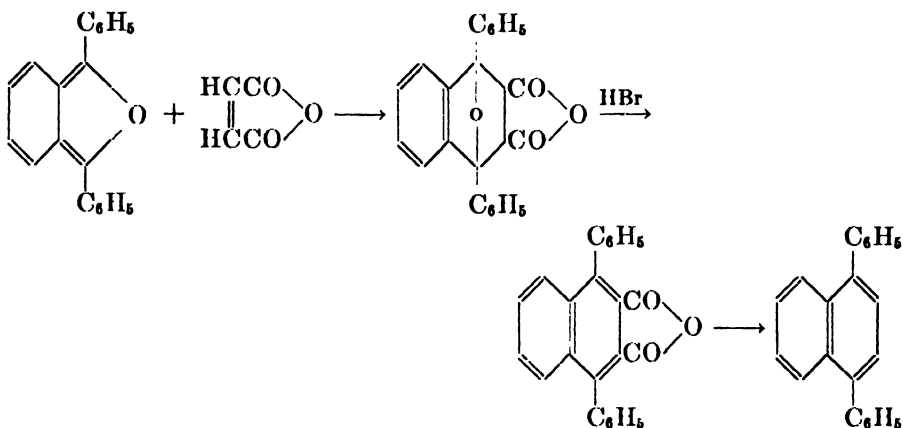
Weiss and his coworkers (353) employed the 1,4-diphenyl-2,3-naphthalic anhydride obtained as an intermediate in the above series of reactions in the synthesis of a difluorenone. The naphthalic anhydride cyclized in the presence of sulfuric acid to give sym-1,2,3,4-o-dibenzoylenenaphthalene (XXI).

XXI   XXII
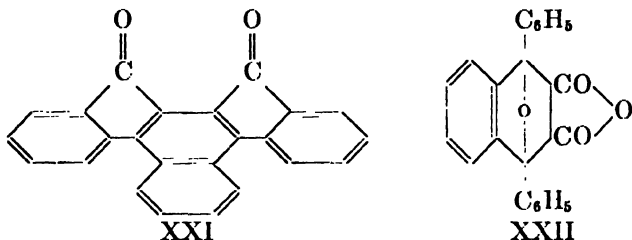
Barnett (71) added maleic anhydride to 1,3-diphenylisobenzofuran to obtain XXII. This reaction proceeds at room temperature in a dichloroethylene solution of the reactants. According to Dufraisse and Priou (188), the adduct obtained at higher temperatures differs from that obtained at room temperature, though both adducts undergo hydrolysis to give the same acid. The room-temperature adduct is stable in the solid state, but dissociation takes place in solvents such as ethyl acetate with formation of limited amounts of the generators. It is indeed remarkable that the aromatic ring of the adduct should revert spontaneously to the cyclohexadiene ring of the isobenzofuran, and especially to a diene containing semicyclic double bonds which ordinarily tend to wander into the ring. Considerations such as these may lead one to wonder if the diene addition reaction has not occurred by some other mechanism, but the degradation of the adduct to 1,4-diphenylnaphthalene by Dufraisse and Priou (187) indicates that such is not the case.

p-Benzoquinone also combines with 1,3-diphenylisobenzofuran to give XXIII which is stable in the solid state, but which dissociates in solution to such a considerable degree that purification by crystallization is difficult (71). Action of hydrogen chloride should give 9,10-diphenyl-1,4-anthraquinone.

Acrolein was added to 1,3-diphenylisobenzofuran by Weiss and his coworkers (353). When the adduct (XXIV) was treated with an acetone solution of potassium permanganate, the oxide bridge was ruptured and the aldehyde group was oxidized, so that the final product was 1,4-diphenyl-2-naphthoic acid. Heating with soda lime partially decarboxylated the acid to 1,4-diphenyl-naphthalene, but a substantial portion cyclized to 3-phenyl-1,2-benzofluorene (XXV).

O C₆H₅   C₆H₅   C₆H₅
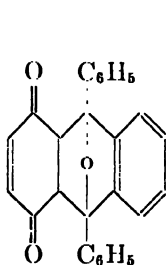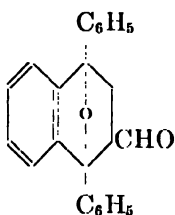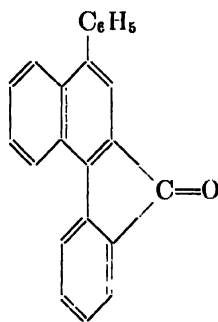
XXIII   XXIV   XXV

The reactions of diene synthesis and oxide-bridge rupture may be conducted in one operation (354). Addition of ethyl cinnamate to 1,3-diphenylisobenzofuran in a medium of alcoholic hydrogen chloride yields 1,3,4-triphenyl-2-naphthoic ethyl ester (XXVI), which is cyclized by sulfuric acid to 1,4-diphenyl-2,3-benzofluorenone (XXVII). If phenol and hydrogen iodide are used for cyclization, the corresponding fluorene is produced.
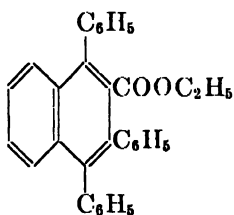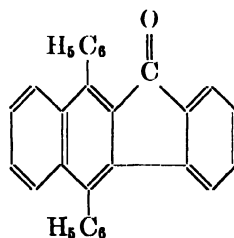
XXVI   XXVII

1,4-Diphenyl-2,3-benzofluorenone may be prepared directly by the reaction of 1,3-diphenylisobenzofuran with indene (354). The adduct first formed dehydrates under the conditions of the experiment to give the fluorenone. This appears to be the sole example observed of the rupture of an oxide bridge by heat alone.

Bergmann (83) added 1,4-naphthoquinone to 1,3-diphenylisobenzofuran, and

obtained 9,10-endo-oxo-9,10-diphenyl-9,9a,10,10a-tetrahydro-11,12-naphtha-cenequinone (XXVIII).
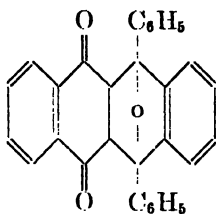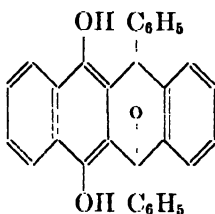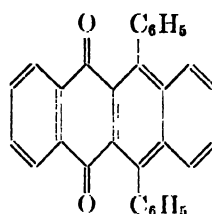
XXVIII	XXIX	XXX

This compound was shown to isomerize when treated with an acetic acid solution of hydrogen bromide; one of the several possible products of isomerization lost 2 moles of water in the process to give 9,10-diphenyl-11,12-naphthacenequinone (XXX), which was isolated from the reaction mixture. The other product isolated from the isomerization reaction was 1,4-diphenyl-1,4-endo-oxo-1,4-dihydro-2,3-benz-9,10-anthraquinol; it may be that the quinol can be converted into XXX by further action of hydrogen bromide.

Dufraisse and Compagnon report (185) the reaction of 1,4-naphthoquinone with 1,3-diphenylisobenzofuran, obtaining the same adduct (XXVIII) as did Bergmann. On treatment with hydrogen chloride or sulfuric acid, they report that the oxide bridge was ruptured and the product obtained by subsequent dehydration was XXX. No mention of XXIX was made. The quinone XXX was made use of in the synthesis of rubrene; XXX was treated with phenyl-magnesium bromide in xylene at elevated temperatures, for no reaction occurred at ordinary temperatures. The dihydroxy compound thus obtained was dehydrated and reduced to rubrene using iron and acetic acid:
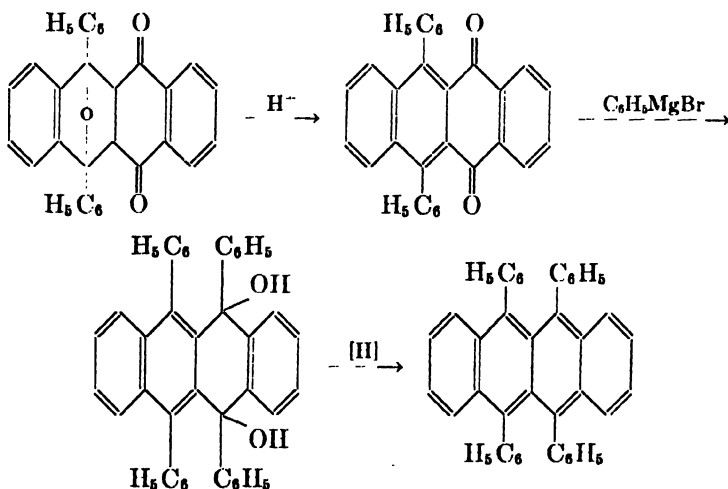
A number of other isobenzofurans have been studied, but only to a limited extent. 1,3-Bis(α-naphthyl)isobenzofuran (355) adds maleic anhydride and

acrolein. The properties of these resulting adducts resemble those of the diphenyl analogs.

1,3-Bis(3,5-dibromo-4-hydroxyphenyl)isobenzofuran (356) adds maleic anhydride or maleic ester in boiling toluene. Hydrogen chloride splits out water and the adducts are thereby aromatized to 1,4-bis(3,5-dibromo-4-hydroxy)-2,3-naphthalic anhydride or ester.

1,3-Bis(p-chlorophenyl)isobenzofuran (6) has been reported to add maleic anhydride.

1,3-Diphenyl-5,6-dimethylisobenzofuran (3) adds maleic anhydride. This addition is so readily reversible that purification is difficult. The adduct is stable in the solid state, but is extensively dissociated in solution.

1,3-Diphenyl-5,6-dimethyl-4,7-dihydroisobenzofuran adds maleic anhydride, and the product (XXXI) contains a 1,4-cyclohexadiene ring.

XXXI
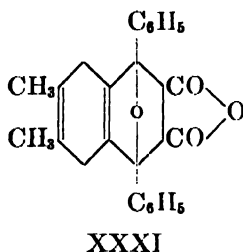
D. Pyrroles

Pyrroles, the heterocyclic nitrogen atom of which occupies a position in the Periodic Table between the corresponding carbon and oxygen atoms of cyclopentadiene and furan, respectively, might be expected to act toward dienophiles as do these other two classes of matter. In no case is this true.

The reaction which would be anticipated is as follows:
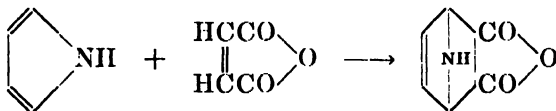
This type of reaction is not observed, and it is always found that heterocyclic dienes which contain nitrogen as a member of the ring show abnormal diene reactions. It is also found that the solvent is an important factor in determining the structure of the main product of the reaction.

Pyrrole itself shows the following reaction (156) with maleic anhydride in an aqueous medium:
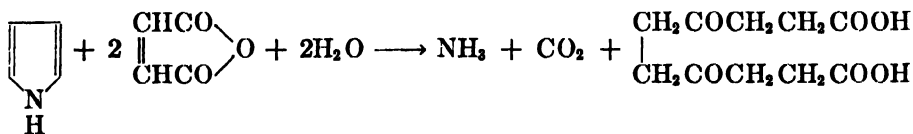
In addition, there is obtained a small amount of 2,5-pyrrolylenedisuccinic acid (XXXII), which lends credence to the following mechanism for the pyrrole reaction:

$$
\begin{array}{c}
\text{pyrrole} + 2\ \overset{\displaystyle CHCO}{\underset{\displaystyle CHCO}{\parallel}}\!\!\!\!>\!O \longrightarrow \\
\end{array}
$$

$$
H_2C\!-\!-\!CH\!-\!-\!CH\!-\!-\!CH_2 \xrightarrow{H_2O}
$$

$$
H_2C\!-\!-\!CH\!-\!-\!CH\!-\!-\!CH_2 \xrightarrow{H_2O}
$$

$$
\underset{HOOC\quad COOH\quad H\quad COOH\quad COOH}{CH_2\!-\!CH\!-\!-\!CH\!-\!-\!CH_2} \xrightarrow{H_2O}
$$

XXXII

$$
NH_3 + HOOCCH_2CH\!-\!\underset{\underset{OH}{|}}{C}\overset{\overset{CH\!-\!CH}{\parallel}}{}\underset{\underset{OH}{|}}{C}\!-\!-CHCH_2COOH \longrightarrow
$$

$$
HOOCCH_2CH\!-\!\underset{\underset{O}{\parallel}}{C}\overset{\overset{CH_2\!-\!CH_2}{|}}{}\underset{\underset{O}{\parallel}}{C}\!-\!CHCH_2COOH \longrightarrow
$$

$$
2CO_2 + \underset{CH_2COCH_2CH_2COOH}{\overset{CH_2COCH_2CH_2COOH}{|}}
$$
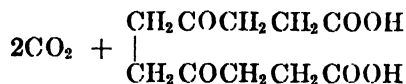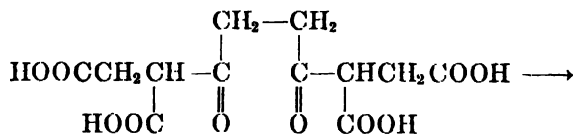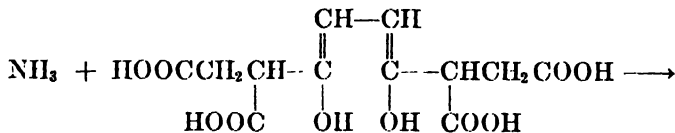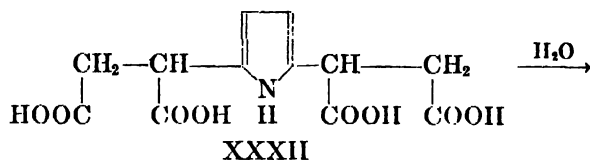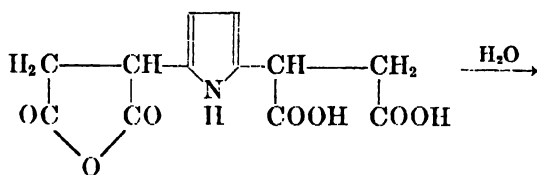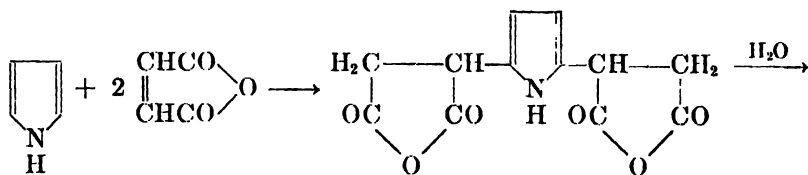
It will be recalled that a somewhat similar reaction is shown by acrolein and furan in the presence of small amounts of sulfur dioxide (page 472).

2-Methylpyrrole reacts somewhat similarly with maleic anhydride in aqueous solution to give 2-methyl-5-pyrrolylsuccinic acid (XXXIII) (156). 1-Methylpyrrole (156) reacts to give the N-methyl derivative of XXXII.

$$
\underset{\underset{H\quad COOH}{N\ \ \ |}}{CH_3}\!\!>\!\!CHCH_2COOH
$$

XXXIII
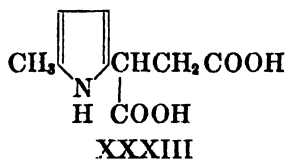
The reactions of pyrroles with acetylenedicarboxylic acid and its esters are also abnormal. In general, they follow one or more of three distinct types:

(A)

(B)

(C)
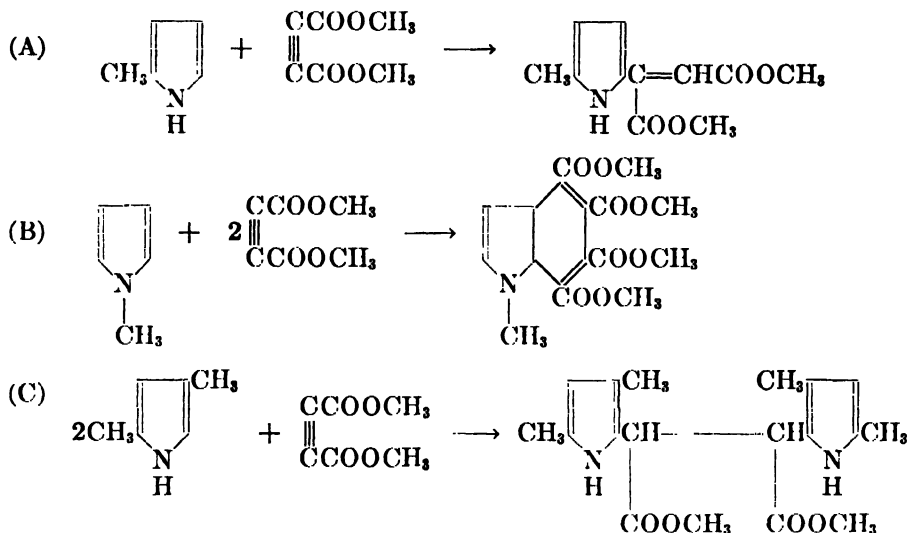
2,3,4-Trimethylpyrrole (155) reacts with dimethyl acetylenedicarboxylate and also with maleic anhydride according to Type A. As indicated in the type reactions, 2-methylpyrrole reacts according to Type A (154, 155, 156), 1-methylpyrrole follows Type B, and 2,4-dimethylpyrrole follows Type C. But when the dienophile is acetylenedicarboxylic acid instead of its dimethyl ester, 1-methylpyrrole follows Type A (155). The ester resulting from the Type B reaction of 1-methylpyrrole may be oxidized with bromine (155) to give XXXIV, which may be saponified and decarboxylated to give N-methylindole in high yield.
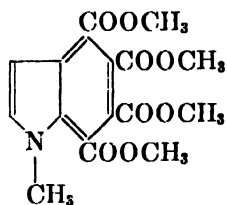
XXXIV

Ethyl 2,4-dimethylpyrrole-5-carboxylate reacts with acetylenedicarboxylic acid to give a product differing in type from all adducts discussed previously (225).

It may be seen that all α-positions are blocked and that substitution can occur only on the lone β-position. One might surmise that substitution occurs preferentially on the α-positions, but can occur on the β-positions if the former are blocked.

2,5-Dimethylpyrrole, 2,3,4-trimethylpyrrole, and 2,4-dimethyl-3-ethyl-

pyrrole react with p-benzoquinone and also with 2,5-dibromo-p-benzoquinone (305) to give adducts of the general formula XXXV, where R is hydrogen or an alkyl group, and X is hydrogen or bromine. The by-product of the reaction is the corresponding quinhydrone or hydroquinone.
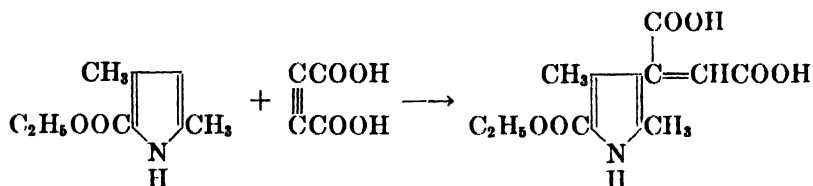
A similar reaction is shown with p-toluquinone (305), but only 1 mole of the pyrrole is involved. The structure of the product is not certain, being either XXXVI or XXXVII; the former is to be preferred tentatively. The inhibiting

XXXV   XXXVI

XXXVII   XXXVIII
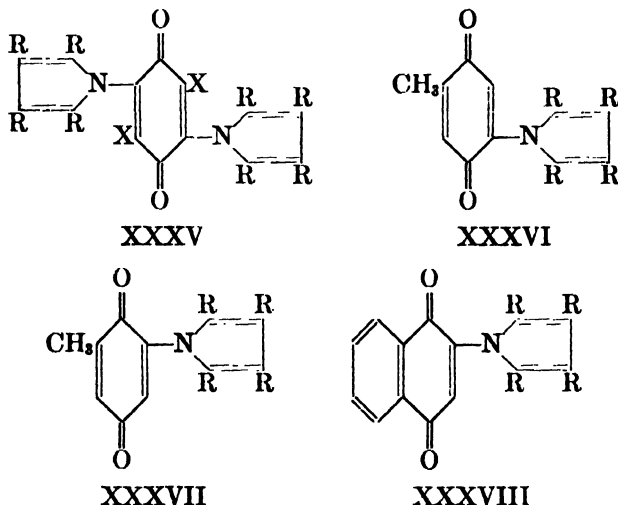
effect of substituents in the p-benzoquinone ring appears to be carried over into these abnormal diene syntheses; it is to be noted that easily removed substituents (such as bromine) do not hinder addition in these reactions.

Addition of the above pyrroles also occurs to 1,4-naphthoquinone, giving XXXVIII.

Azibutanone (163) reacts with pyrrole to eliminate nitrogen and to form 2,3-dihydro-2,3-(1-acetyl)ethylidenepyrrole:
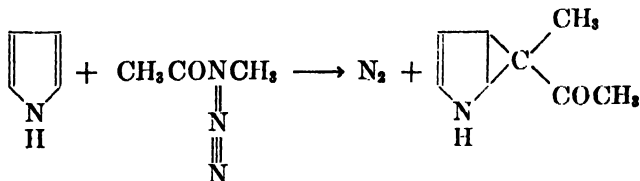
E. Imidazoles

Imidazoles react with acetylenedicarboxylic esters in a manner similar to that of the pyrroles. Thus 4-methylimidazole reacts according to Type A to give one of the two possible isomers (155); it is not certain which isomer is produced.
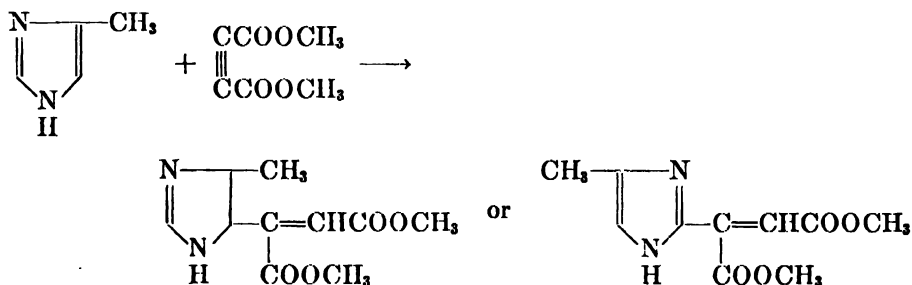
$$\text{II} \quad + \quad \begin{array}{c} \text{CCOOCH}_3 \\ \parallel \\ \text{CCOOCH}_3 \end{array} \longrightarrow$$

$$\begin{array}{c} \text{N}\text{---CH}_3 \\ \parallel \quad \text{---C=CHCOOCH}_3 \\ \text{N} \quad \text{COOCH}_3 \\ \text{H} \end{array} \quad \text{or} \quad \begin{array}{c} \text{CH}_3\text{---N} \\ \text{---C=CHCOOCH}_3 \\ \text{N} \quad \text{COOCH}_3 \\ \text{H} \end{array}$$

1-Methylimidazole reacts (155) according to Type C:

$$2 \quad \begin{array}{c} \text{N} \\ \parallel \\ \text{N} \\ \text{CH}_3 \end{array} \quad + \quad \begin{array}{c} \text{CCOOCH}_3 \\ \parallel \\ \text{CCOOCH}_3 \end{array} \longrightarrow \begin{array}{c} \text{N} \quad \text{COOCH}_3 \quad \text{N} \\ \text{---CH---CH---} \\ \text{N} \quad \text{CH}_3\text{OOC} \quad \text{N} \\ \text{CH}_3 \qquad\qquad \text{CH}_3 \end{array}$$

1,2-Dimethylimidazole reacts (155) according to Type B:

$$\begin{array}{c} \text{---N} \\ \text{N} \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \quad + \quad 2 \begin{array}{c} \text{CCOOCH}_3 \\ \parallel \\ \text{CCOOCH}_3 \end{array} \dashrightarrow \begin{array}{c} \text{COOCH}_3 \\ \text{---N} \diagup \diagdown \text{COOCH}_3 \\ \text{---COOCH}_3 \\ \text{N} \diagdown \text{COOCH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{array}$$
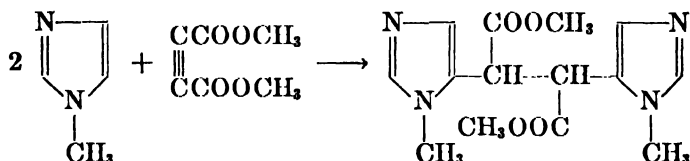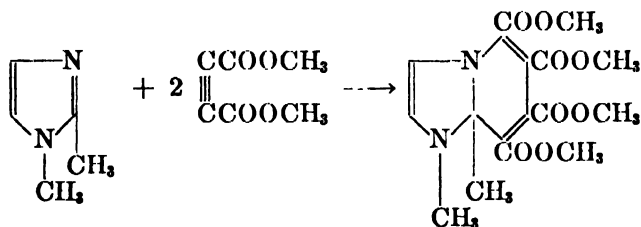
Bromine treatment of the product from 1,2-dimethylimidazole gives XXXIX, which may be saponified and decarboxylated to α-picoline (XL).

$$\begin{array}{c} \text{COOCH}_3 \\ \text{N} \diagup \diagdown \text{COOCH}_3 \\ \text{CH}_3 \diagup \diagdown \text{COOCH}_3 \\ \text{COOCH}_3 \end{array} \qquad \begin{array}{c} \diagup \diagdown \\ \text{N} \diagdown \text{CH}_3 \end{array}$$

XXXIX   XL
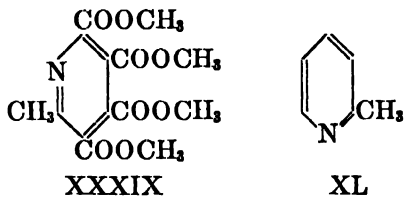
F. Indoles and carbazole

Carbazole is the dibenzolog of pyrrole; it does not react with maleic anhydride. A method of separation of anthracene from carbazole in the coal-tar anthracene fraction is based on this fact (303).

Indoles, the monobenzologs of pyrroles, react with maleic anhydride, acetylenedicarboxylic esters, and *p*-benzoquinone (143) in highly abnormal manners. For example, skatole reacts with maleic anhydride as follows:
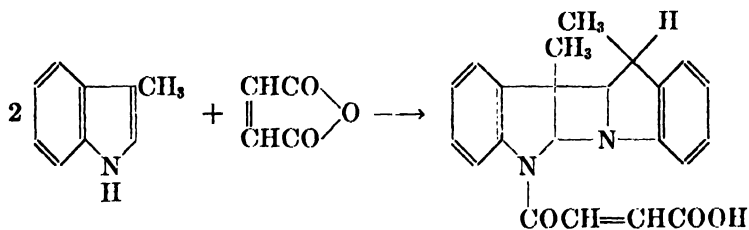
Indole reacts in a manner identical with skatole, but α-methylindole reacts in a most original manner to give three products:
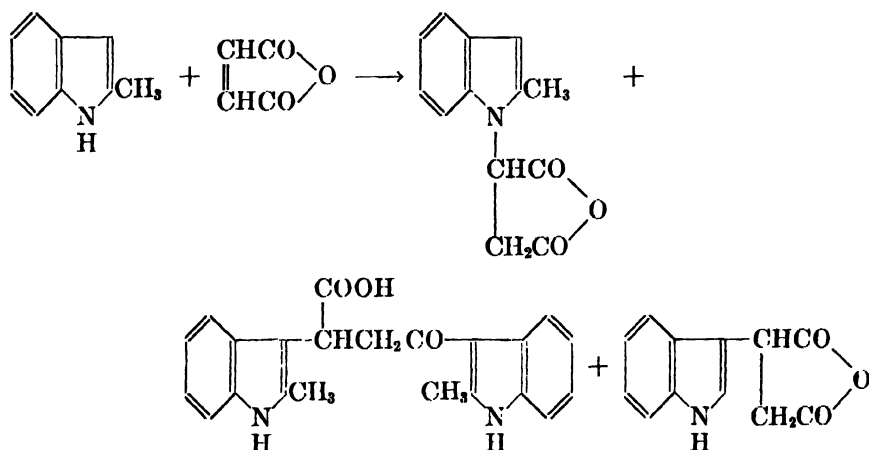
1,2-Dimethylindole reacts in a manner similar to α-methylindole, but does not form the *N*-substituted type of compound.
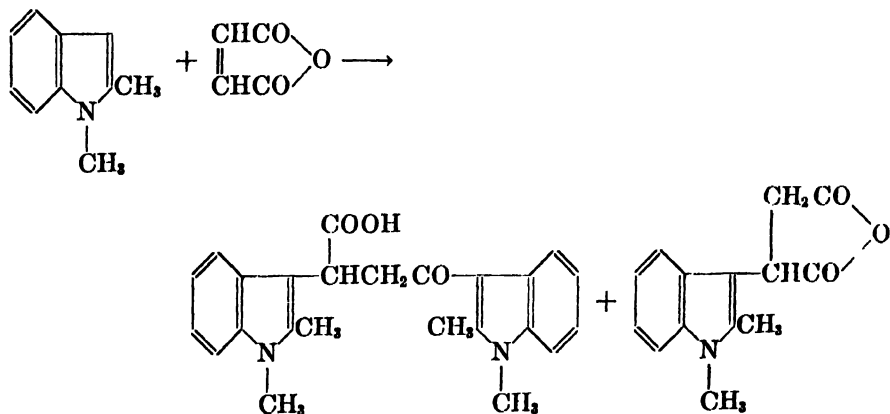
It reacts somewhat similarly with the dimethyl ester of acetylenedicarboxylic acid.
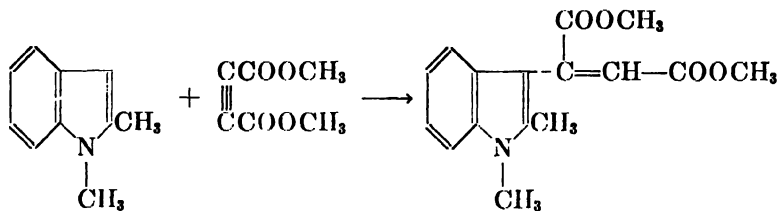
2-Methylindole (143, 294) reacts with maleic anhydride to give products analogous to those from 1,2-dimethylindole and, in addition, forms a third compound (XLI). Reaction with p-benzoquinone gives XLII, which is analogous to one of the maleic anhydride products.

XLI   XLII
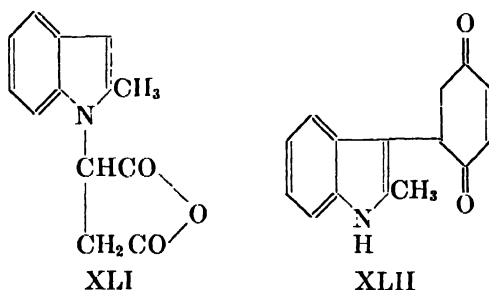
Unlike the pyrroles, azibutanone is without action on indole, skatole, and 2-methylindole (163).

G. Pyridine, its derivatives, and its benzologs

The reactions of pyridine as a diene may be regarded, on initial consideration, as being those of the alternating double bonds of the Kekulé structure. However, the reaction products of this as well as of the other nitrogenous heterocycles are not those anticipated from a consideration of the simple diene–dienophile reaction. The nature of the products isolated may, however, offer a clue as to the mechanism of diene reactions in general.

The reaction products of pyridine and acetylenedicarboxylic dimethyl ester differ according to the nature of the solvent employed. In acetic acid solution, the sole reaction observed is trimerization of the ester to give hexamethyl mellitate (135, 142, 160); apparently the trimerization is catalyzed by pyridinium ion. In ether solution, an entirely different reaction occurs with formation of condensed ring systems containing nitrogen as one of the bridge atoms (140, 141, 164):

$$- \rightarrow \text{(structure, COOCH}_3\text{, COOCH}_3\text{, COOCH}_3\text{, COOCH}_3\text{)} + \text{(structure, N}^+\text{, COOCH}_3 \times 4\text{)} + \text{(structure, N}^+\text{, COOCH}_3 \times 3\text{, COO}^-\text{)}$$
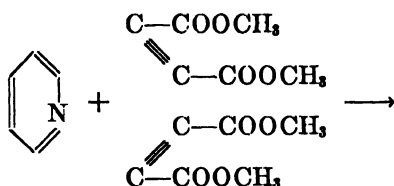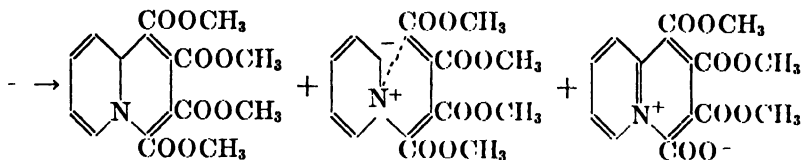
In methanol solution at 0°C., the product differs from that obtained in ether (164).

$$\text{(pyridine)} + 2 \begin{array}{c} \text{CCOOCH}_3 \\ \parallel \\ \text{CCOOCH}_3 \end{array} \longrightarrow \text{(structure with OCH}_3, \text{CHCOOCH}_3, \text{COOCH}_3, \text{COOCH}_3\text{)}$$
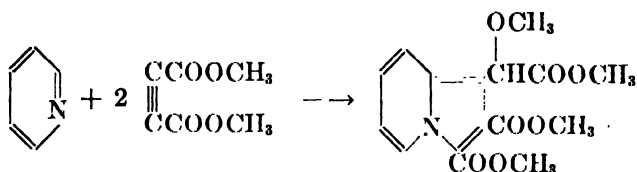
At higher temperatures, or by treatment of the above product with bromine in methanol solution, there is also obtained trimethyl indolizintricarboxylate (XLIII).

In the interests of nomenclature, it must be stated that the parent compounds XLIV and XLV are named quinizolin and indolizin, respectively. In the
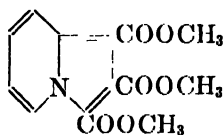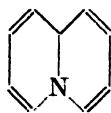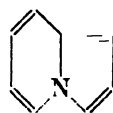
XLIII   XLIV   XLV

literature of Diels and Alder, tetramethyl quinizolin-1,2,3,4-tetracarboxylate (XLVI) is referred to as "the yellow substance", the carbide-type of intermediate (XLVII) is referred to as "the red substance", and the zwitter ion (XLVIII) is named "Kashimoto's Compound". The chemistry of these substances has been
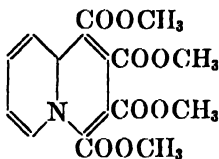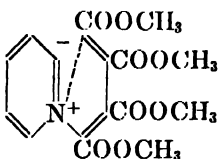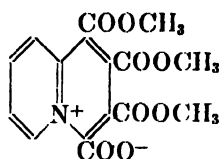
XLVI   XLVII   XLVIII

investigated extensively by Diels and his collaborators. The proof of the structure of XLVI is based mainly on oxidative degradation (140, 142) to α-picolinic acid N-oxide. Successive action of bromine or nitric acid and pyridine on XLVI gives rise to Kashimoto's compound (XLVIII). Other typical reaction sequences include the degradation of XLVI to norlupine (142), the degradation of XLIII to octahydroindolizin (164), and the degradation of XLVI to an isomer of norlupinane (171).

Adduct XLIX, from pyridine and acetylenedicarboxylic dimethyl ester in methanol solution at 0°C., may be reduced catalytically to a tetrahydro compound. It is attacked by acetic anhydride, suffering replacement of a

XLIX   L   LI
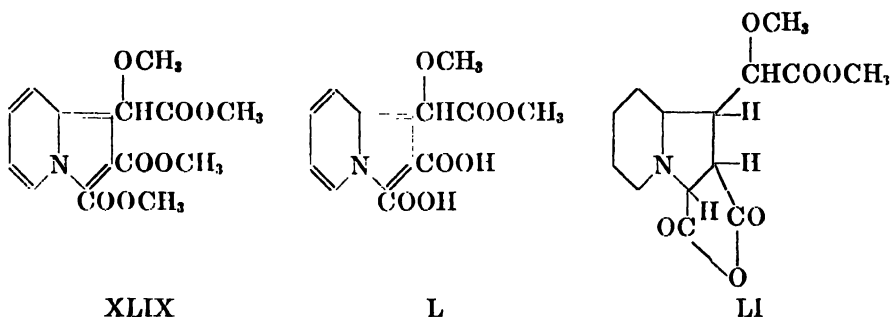
—COOCH₃ group by an acetyl group (164).   XLIX is saponifiable to a dicar-
boxylic acid (L), hydrogenation of which followed by dehydration with acetic
acid yields an anhydride (LI).   If hydrogenation precedes saponification, the
final product is the acid (LII), which does not form an anhydride because the
two carboxyl groups are *trans* to each other (164).

LII   LIII   LIV
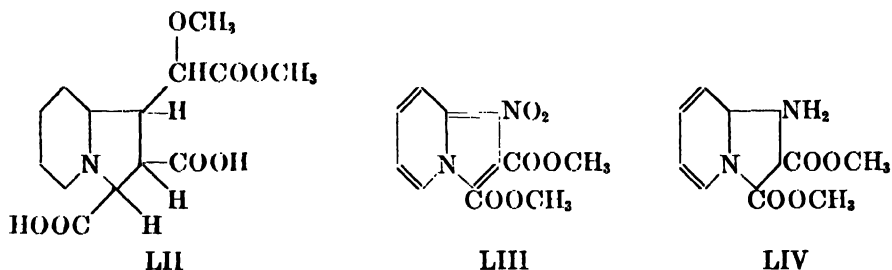
The —CH(OCH₃)COOCH₃ side chain of XLIX is readily removed by action
of an acetic acid solution of nitric acid to give LIII, which can be easily reduced
to give LIV.

LV   LVI

LVII   LVIII
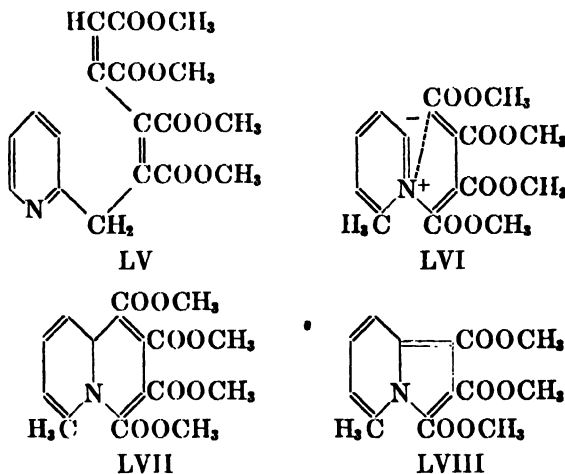
α-Picoline reacts with acetylenedicarboxylic dimethyl ester in ether solution
at 0°C. to give a red, stable adduct of formula LV.   There is also produced a

yellow, labile, carbide-type of intermediate (LVI), which is stabilized by heat or by acetic acid to give the orange compound (LVII). Oxidation of LVII with sodium dichromate in acetic acid gives an indolizin compound (LVIII), further oxidation of which gives 6-methyl-2-picolinic acid N-oxide (167).

The reaction of 2-stilbazole (165) with acetylenedicarboxylic dimethyl ester in ether solution proceeds to give an orange labile compound (LIX), which is converted by heat into the first stable addition product (LX). Further heating produces the second stable addition product (LXI), which is unique in its possession of an angular group. Unlike the labile orange product (LIX) or the first stable addition product (LX), LXI does not seem to be convertible into the

LIX   LX   LXI
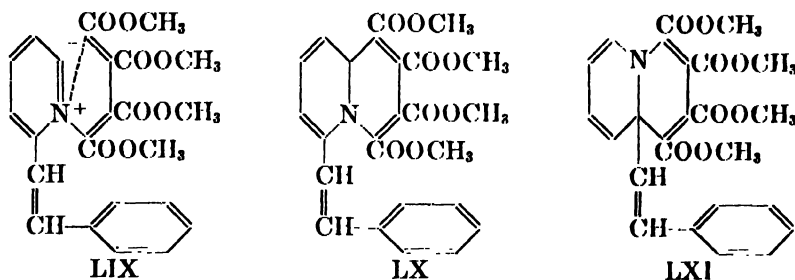
indolizin type of compound (LXII) by boiling in acetic acid, nor does it seem to be convertible into LXIII by sodium dichromate in acetic acid.

LXII   LXIII
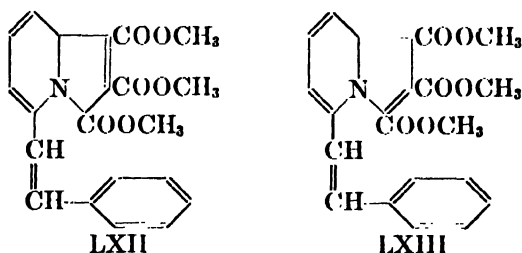
Quinoline (141, 155) reacts with acetylenedicarboxylic dimethyl ester in ether solution much as does pyridine, for it forms a yellow labile product (LXIV), which is transformed by heat into red tetramethyl 5,6-benzquinizolin-1,2,3,4-tetracarboxylate (LXV). Like the corresponding quinzolin derivative, LXV is easily oxidized by chromic or dilute nitric acid to the indolizin derivative (LXVI).

LXIV   LXV   LXVI
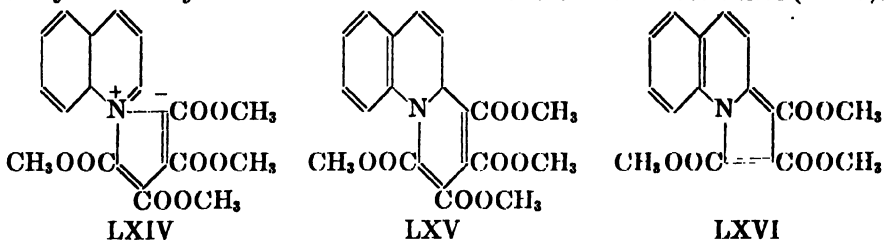
α-Quinaldine (155) reacts with an ether solution of dimethyl acetylenedicarboxylate to give a labile compound of anticipated formula (LXVII). It is

heat-stabilized to give a compound first thought to be LXIX, but this was shown to be erroneous, for the compound was LXVIII. During the heat stabilization LXX is also formed through condensation with the reactive methyl group, followed by rearrangement.

LXVII

LXVIII

LXIX

LXX
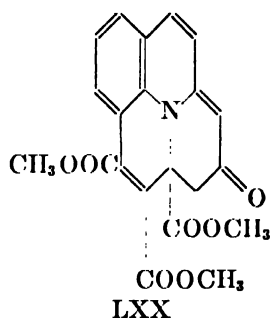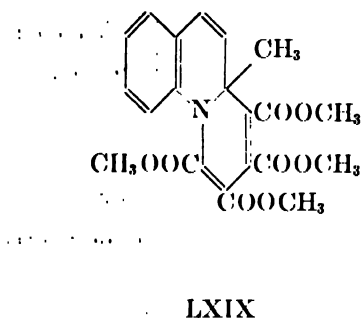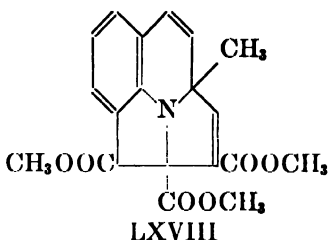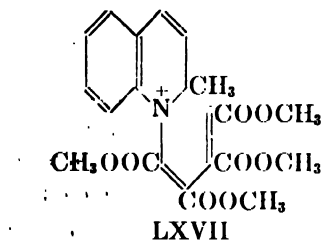
2-Styrylquinoline (86) appears to form only the maleate on treatment with acetylenedicarboxylic dimethyl ester.

Isoquinoline (155, 159) reacts with acetylenedicarboxylic dimethyl ester in ether solution to give, mainly, an orange-yellow labile adduct to which structure LXXI has been assigned. A small amount of a red isomer is also produced, to which structure LXXII has been assigned. LXXII is heat-stabilized to LXXIII, while LXXI is heat-stabilized to a mixture of LXXIII and LXXIV.

LXXI

LXXII

LXXIII

LXXIV
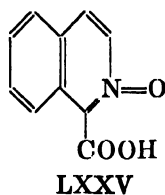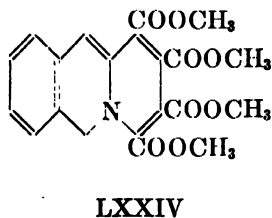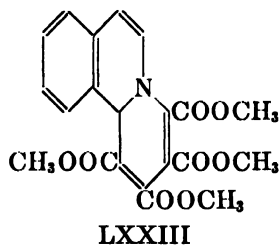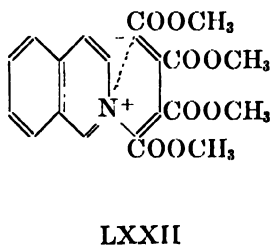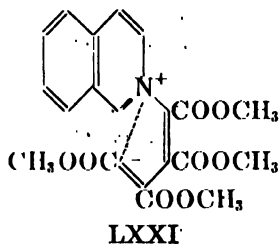
LXXV

The compound LXXIII, like its pyridine and quinoline analogs, can be degraded oxidatively to LXXV.

9-Phenanthridine (174) acts much in the same manner as pyridine and quinoline when treated with acetylenedicarboxylic dimethyl ester. The first product is a labile adduct (LXXVI); the stable adduct (LXXVII) is obtained
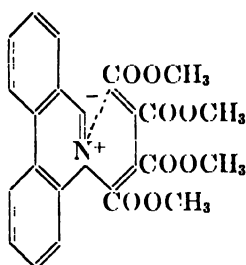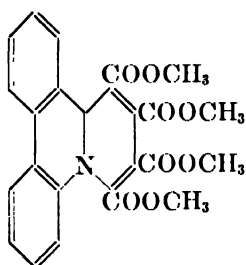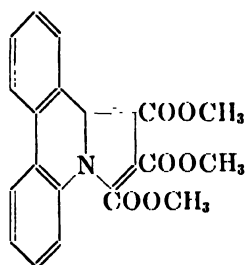
LXXVI   LXXVII   LXXVIII

by boiling LXXVI first with quinoline and then with ethyl alcohol. Crystallization of LXXVI from ether or acetonitrile gives the indolizin compound (LXXVIII). Crystallization from methanol gives LXXIX.
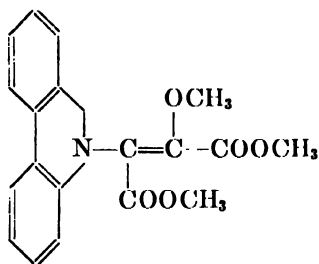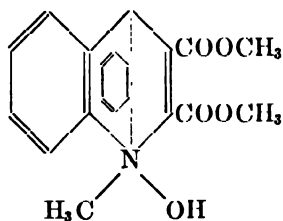
LXXIX   LXXX

Acridine was treated with maleic anhydride by Barnett (72), who failed to obtain an adduct. Diels and his students (173) obtained various products with acridine and acetylenedicarboxylic dimethyl ester. Refluxing the two reactants in methanol for two days gives the bridged quaternary hydroxide (LXXX); in addition, 1 to 2 per cent of a light yellow compound (LXXXI) is also formed. Ethanol forms the bridged ethylacridonium hydroxide corresponding to LXXX. When dioxane is the solvent, 20 to 30 per cent of the product is LXXXI, which probably results by atmospheric oxidation on evaporation of the solvent. The remainder of the dioxane product is the ruby-red labile adduct (LXXXII).

In ether solution, the product is mainly the *trans*-isomer of LXXXI, although some of the *cis*-isomer is formed. The yield of LXXXII is very small in this case. If perhydrol is incorporated into the reaction mixture which employs methanol as the solvent, a nearly quantitative yield of the *cis*-form of LXXXI results. Atmospheric oxidation of LXXX also results in formation of the *cis*-form of LXXXI. Crystallization of the *trans*-isomer of LXXXI from pyridine gives the *cis*-isomer, and oxidation of the ruby-red labile adduct

(LXXXII) with perhydrol gives a 90 per cent yield of the *cis*-form of LXXXI plus small amounts of LXXXIII.

LXXXI   LXXXII   LXXXIII
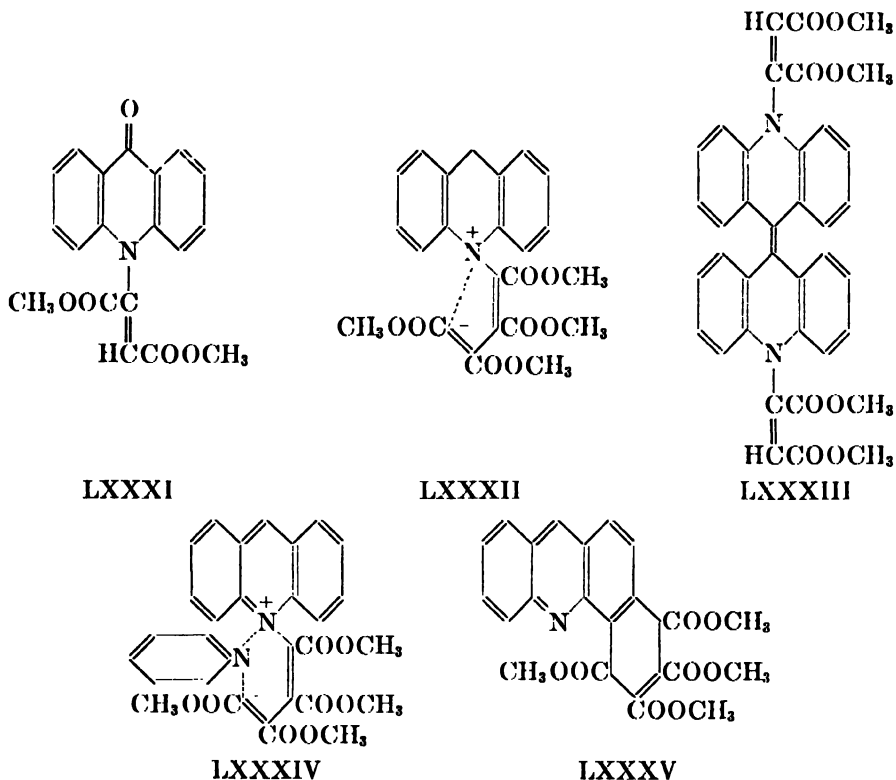
LXXXIV   LXXXV

Pyridine forms a complex with LXXXII, to which structure LXXXIV has been given.

An abnormal stable adduct, LXXXV, is formed by dissolving LXXXII in concentrated sulfuric acid, followed by dilution with water.

XIV. MISCELLANEOUS NITROGEN COMPOUNDS

The miscellaneous nitrogen compounds to be discussed under this heading are not dienic, but were studied in connection with the heterocyclic nitrogen-containing dienes. Their reactions are quite similar to those of the pyrroles and pyridines.

A. Hydrazines

A few hydrazines were studied by Diels and his coworkers; the first to be considered is *sym*-diphenylhydrazine (hydrazobenzene). It reacts with acetyenedicarboxylic dimethyl ester (168) in methanol solution:
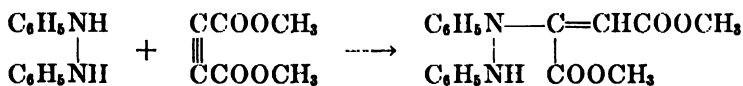
Nitric acid acts upon the adduct:

$$\begin{array}{cc} C_6H_5N\!-\!C\!=\!CHCOOCH_3 \\ |\quad\quad| \\ C_6H_5NH\ \ COOCH_3 \end{array} \xrightarrow{HNO_3} \begin{array}{c} COOCH_3 \\ | \\ C \\ \diagup\quad\diagdown \\ C_6H_5N\quad\quad CH \\ |\quad\quad\quad| \\ C_6H_5N\!-\!\ \ C\!=\!O \end{array} +\ CH_3OH$$
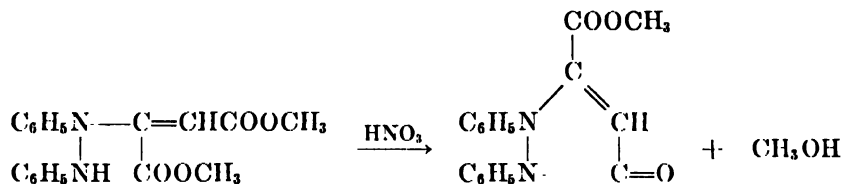
If the formation of the adduct is conducted in acetic acid solution instead of methanol, the second compound (produced above by means of nitric acid) is formed directly.

The tautomeric form of oxalacetic ester reacts with hydrazobenzene directly to give the same compound:

$$\begin{array}{c} C_6H_5NH \\ | \\ C_6H_5NH \end{array} + \begin{array}{c} O \\ \diagup\!\!\diagup \\ C_6H_5\!-\!C \\ \diagdown \\ CH \\ \diagup\!\!\diagup \\ HO\!-\!C \\ \diagdown \\ COOCH_3 \end{array} \ \ \text{---} \rightarrow$$

$$H_2O\ +\ CH_3OH\ + \begin{array}{c} O \\ \| \\ C \\ \diagup\quad\diagdown \\ C_6H_5N\quad\quad CH \\ |\quad\quad\quad\| \\ C_6H_5N\!-\quad CCOOCH_3 \end{array}$$
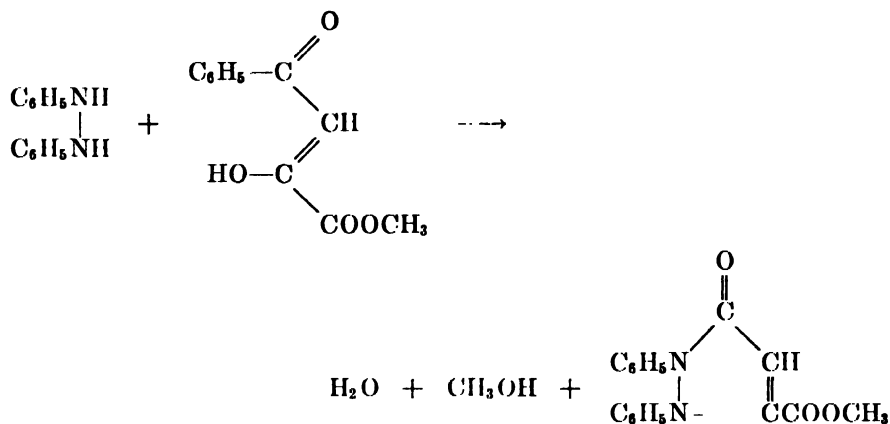
The adducts undergo a number of reactions, two of the most important being the conversions to indole and quinoline derivatives. Heating in xylene yields indole derivatives, while heat alone or heating in pyridine or dimethylaniline yields quinoline derivatives:

$$\begin{array}{c} C_6H_5N\!-\!C\!=\!CHCOOCH_3 \\ |\quad\quad| \\ C_6H_5NH\ \ COOCH_3 \end{array} \xrightarrow{\text{xylene}} C_6H_5NH_2\ + \ \text{[indole-COOCH}_3\text{ derivative]}$$

$$\begin{array}{c} C_6H_5N\!-\!C\!=\!CHCOOCH_3 \\ |\quad\quad| \\ C_6H_5NH\ \ COOCH_3 \end{array} \ \text{---} \rightarrow \ \text{[quinoline derivative]}$$
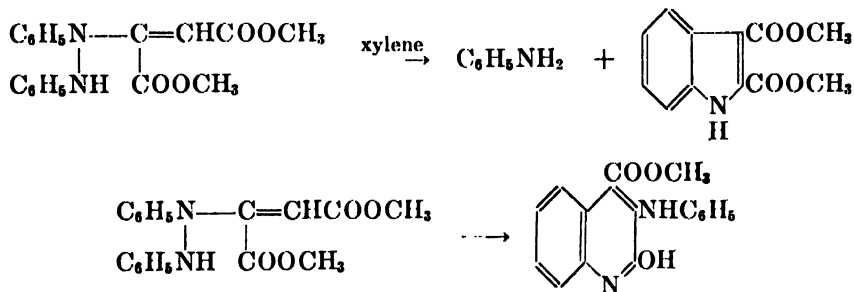
In methanol solution, p,p'-hydrazotoluene and N-phenyl-N'-benzylhydrazine (169) give compounds corresponding to that from hydrazobenzene and acetylene-dicarboxylic dimethyl ester in methanol solution. Analogous compounds are also formed by *sym*-dibenzylhydrazine and tribenzylhydrazine.

Unsymmetrical benzylphenylhydrazine also gives an analogous adduct in cold methanol; the adduct is, however, more labile than the adducts from hydrazines with one or two substituents on each nitrogen atom.   In hot water, the adduct forms the indole type with loss of ammonia:
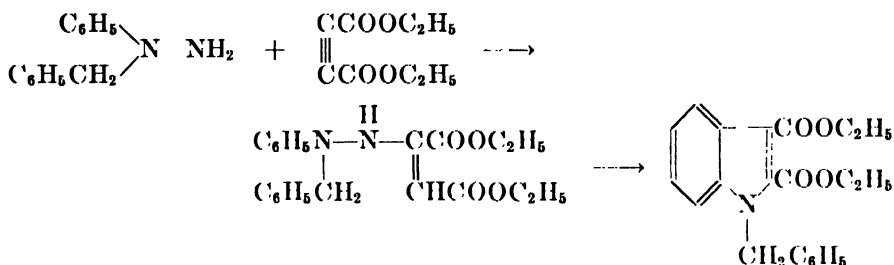
1-Phenyl-1,2-dibenzylhydrazine resembles both pyridine and the above hydrazines in its reaction with acetylenedicarboxylic dimethyl ester, giving a mixture of I and II.

I (yellow)

II (white)

III

IV
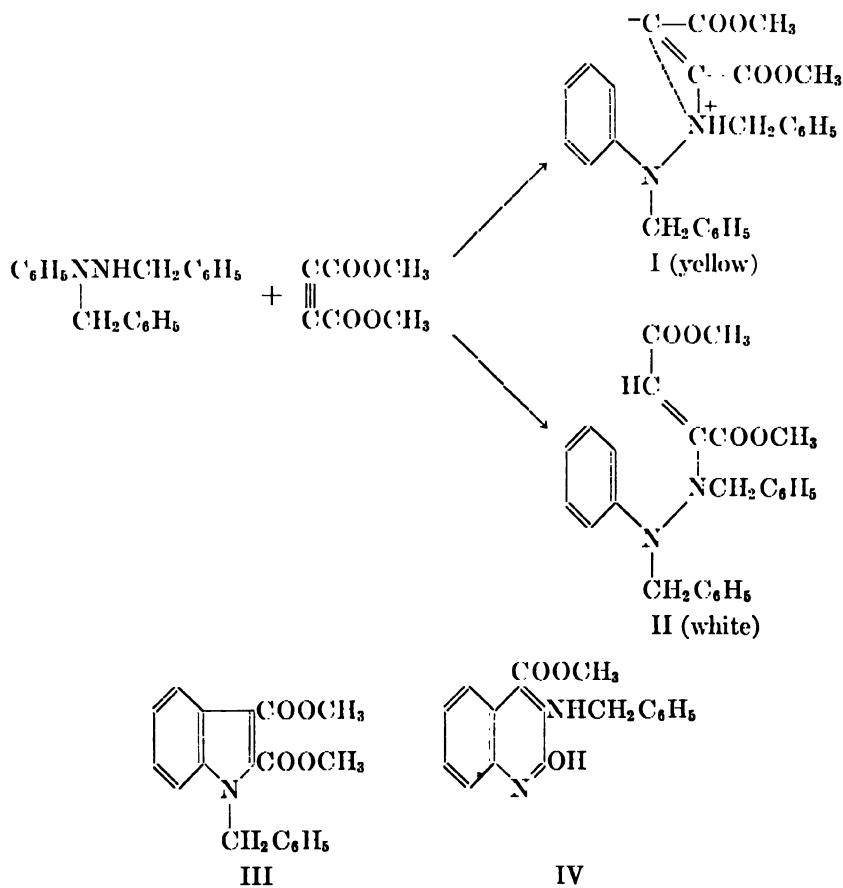
Both I and II give indole and quinoline types. When boiled in xylene, they both give III; when boiled in pyridine, they both give IV.

B. Azibutanone

The reactions of azibutanone, $CH_3COC(CH_3)=N=N$, with pyrroles have been discussed earlier. While it reacts with this class of compounds, it does not react with its benzologs, such as indole and skatole. It also shows no reaction with aliphatic dienes or monomeric cyclopentadiene. It reacts violently with acetylenedicarboxylic ester and with azodicarboxylic ester:
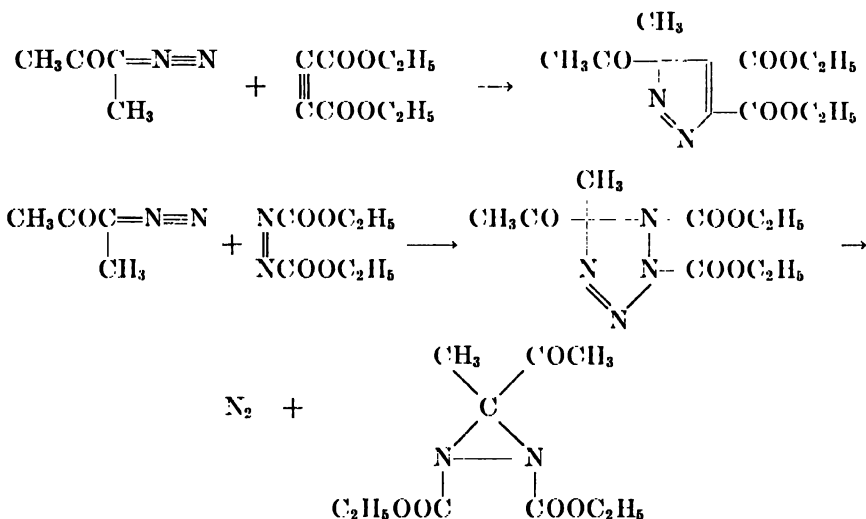
Azibutanone also reacts with the highly active double bond of the bicycloheptene derivatives; for example, the reaction with cyclopentadiene dimer is as follows:
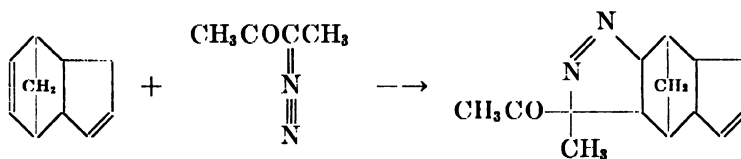
The adduct loses nitrogen on vacuum distillation:
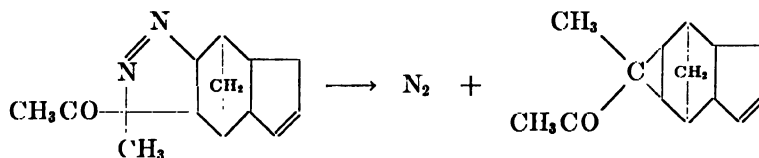
C. Phenyl azide

Phenyl azide reacts with the double bond of bicycloheptene derivatives; indeed, the reaction is almost specific for this ring system and was much used by

Alder and Stein in the proof of structure of the polymers of cyclopentadiene. With the trimer of cyclopentadiene, for example, it reacts as follows:

$$\text{(cyclopentadiene trimer structure)} \quad + \quad C_6H_5N{=}N{\equiv}N \quad \longrightarrow \quad \text{(triazoline adduct structure with } C_6H_5)$$
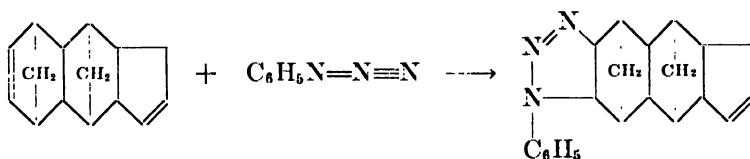
XV. MISCELLANEOUS DIENE SYNTHESES

A. Dimerizations of carbonylenic dienophiles

Alder and his coworkers have recently (380, 381, 383) published a series of papers on the dimerizations of α,β-unsaturated aldehydes and ketones. Diene syntheses of this type are unique in that the function of the diene is played by the grouping $C{=}C{-}C{=}O$ instead of $C{=}C{-}C{=}C$.

This type of diene synthesis may be illustrated by the dimerizations of acrolein (383), methyl vinyl ketone (380), crotonaldehyde (381), and acrylophenone (381). The structures of the dimers of acrolein and of methyl vinyl ketone have been proved, while the structures of the dimers of the other two ketones have not been elucidated conclusively as yet. The reactions involved are the following:

$$\begin{array}{c}
\text{CH}_2 \\
\text{HC} \\
\text{HC} \\
\text{O}
\end{array}
\quad + \quad
\begin{array}{c}
\text{CH}_2 \\
\text{CHCHO}
\end{array}
\quad \longrightarrow \quad
\begin{array}{c}
\text{CH}_2 \\
\text{HC} \quad \text{CH}_2 \\
\text{HC} \quad \text{CHCHO} \\
\text{O}
\end{array}$$

$$\begin{array}{c}
\text{CH}_2 \\
\text{HC} \\
\text{CH}_3\text{C} \\
\text{O}
\end{array}
\quad + \quad
\begin{array}{c}
\text{CH}_2 \\
\text{CHCOCH}_3
\end{array}
\quad \longrightarrow \quad
\begin{array}{c}
\text{CH}_2 \\
\text{HC} \quad \text{CH}_2 \\
\text{CH}_3\text{C} \quad \text{CHCOCH}_3 \\
\text{O}
\end{array}$$

$$\begin{array}{c}
\text{CH}_3 \\
\text{CH} \\
\text{HC} \\
\text{HC} \\
\text{O}
\end{array}
\quad + \quad
\begin{array}{c}
\text{CHCH}_3 \\
\text{CHCHO}
\end{array}
\quad \longrightarrow \quad
\begin{array}{c}
\text{CH}_3 \\
\text{CH} \\
\text{HC} \quad \text{CHCH}_3 \\
\text{HC} \quad \text{CHCHO} \\
\text{O}
\end{array}$$

$$\begin{array}{c}
\text{CH}_2 \\
\text{HC} \\
\text{C}_6\text{H}_5\text{C} \\
\text{O}
\end{array}
\quad + \quad
\begin{array}{c}
\text{CH}_2 \\
\text{CHCOC}_6\text{H}_5
\end{array}
\quad \longrightarrow \quad
\begin{array}{c}
\text{CH}_2 \\
\text{HC} \quad \text{CH}_2 \\
\text{C}_6\text{H}_5\text{C} \quad \text{CHCOC}_6\text{H}_5 \\
\text{O}
\end{array}$$
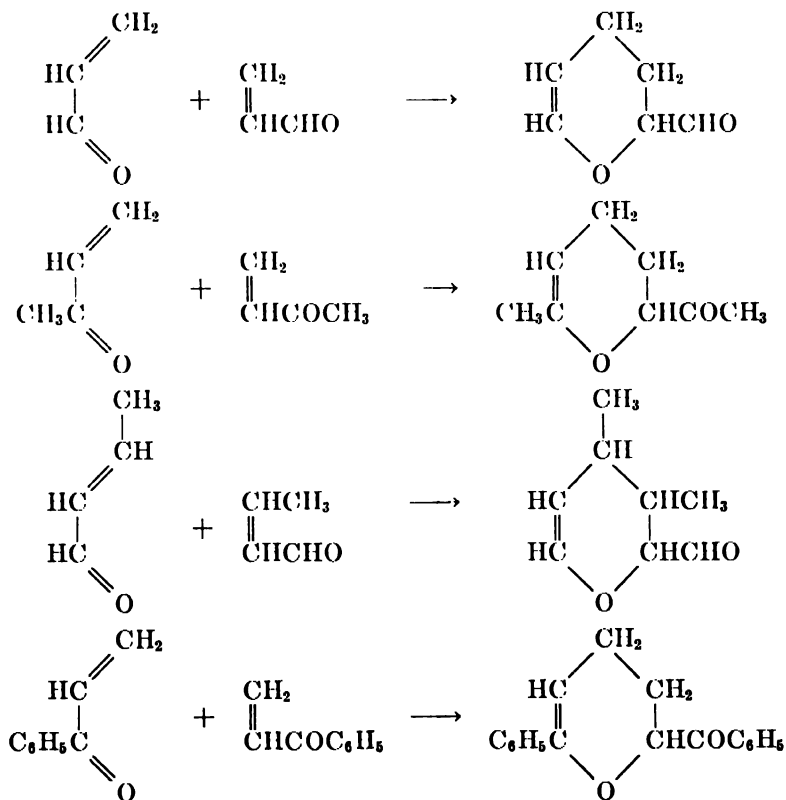
Addition occurs in a manner so that the RCO— group of the dimer is always ortho to the ring oxygen atom, and never meta (381) (for a novel example, see reference 416).

B. Reverse diene syntheses[3]

There are a number of compounds which, when heated strongly, decompose into a diene and an olefinic compound, although the diene and olefin have not been observed to recombine to give the original compound. For want of a better term, these are called reverse diene syntheses.

Perhaps the best known of these reverse diene syntheses is the Kistiakowsky (414) hot-wire method of producing butadiene from cyclohexene:

$$
\begin{array}{ccc}
\underset{\substack{H_2 \\ C}}{\diagup\diagdown} & & \underset{\substack{H_2 \\ C}}{\diagup\diagup} \\
HC\quad CH_2 & \longrightarrow & HC\quad CH_2 \\
\| \quad | & & \quad + \quad \| \\
HC\quad CH_2 & & HC\quad CH_2 \\
\diagdown\diagup & & \diagdown\diagdown \\
\underset{H_2}{C} & & \underset{H_2}{C}
\end{array}
$$
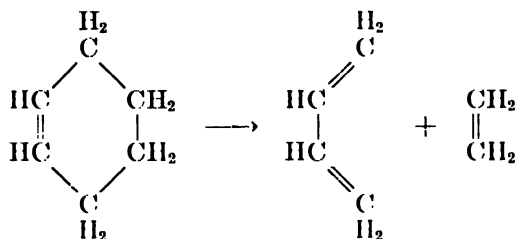
The advantage of the hot-wire method over other pyrolytic methods is that cracking is accomplished without use of an inert gas and without formation of polymeric material. If the pyrolysis is conducted by use of a hot tube, the butadiene, cyclohexene, and ethylene interact and considerable quantities of polymeric materials are obtained. This interaction may be largely avoided by diluting the charged cyclohexene with an inert gas, which is usually steam (392, 427).

Homologs of cyclohexene have likewise been subjected to pyrolysis to give a diene and an olefin. These pyrolyses were conducted using a hot tube and a

$$
\begin{array}{ccc}
\underset{\substack{H_2 \\ C}}{\diagup\diagdown} & & \underset{\substack{H_2 \\ C}}{\diagup\diagup} \\
CH_3C\quad CH_2 & \longrightarrow & CH_3C\quad CH_2 \\
\| \quad | & & \quad + \quad \| \\
HC\quad CH_2 & & HC\quad CH_2 \\
\diagdown\diagup & & \diagdown\diagdown \\
\underset{H_2}{C} & & \underset{H_2}{C}
\end{array}
$$

$$
\begin{array}{ccc}
\underset{\substack{H_2 \\ C}}{\diagup\diagdown} & & \underset{\substack{H_2 \\ C}}{\diagup\diagup} \\
HC\quad CH_2 & \longrightarrow & HC\quad CH_2 \\
\| \quad | & & \quad + \quad \| \\
HC\quad CHCH_3 & & HC\quad CHCH_3 \\
\diagdown\diagup & & \diagdown\diagdown \\
\underset{H_2}{C} & & \underset{H_2}{C}
\end{array}
$$
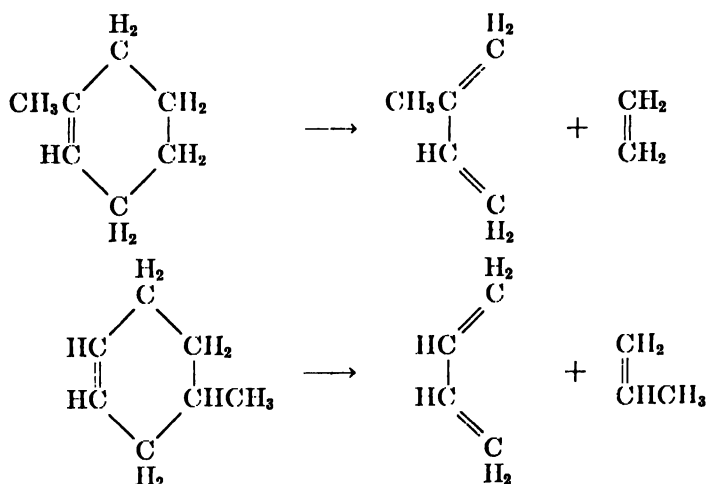
[3] Suggested by Dr. A. O. Rogers. Subsequently, Butz (411) has reversed the decomposition of cyclohexane to butadiene and ethylene.
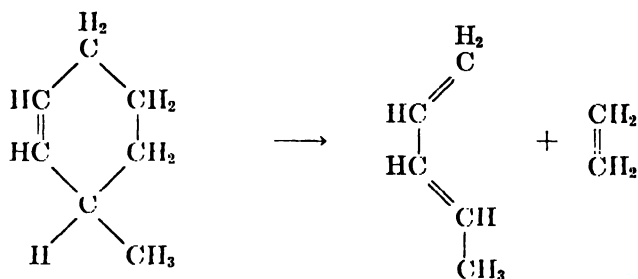
diluting gas. Compounds thus studied are 1-methyl-1-cyclohexene (392, 427), which yields isoprene and ethylene, 4-methyl-1-cyclohexene (427), which yields butadiene and propylene; and 3-methyl-1-cyclohexene (392), which yields ethylene and piperylene.

There are certain other examples known of reverse diene syntheses, but these cannot be reviewed because of current patent situations.

XVI. MECHANISM AND STEREOCHEMISTRY OF THE DIENE SYNTHESIS

A. Postulate of mechanism

This section will deal with the theory of addition and the stereochemical effects observed in the diene synthesis.

Little appears to be known concerning the electronic changes and intermediates formed in the diene synthesis. The transient yellow color observed during the addition of maleic anhydride to a diene and similar transient colors observed in other diene syntheses almost certainly indicate that reactive intermediates, possibly free radicals, are involved in the reaction. A suggestion as to the constitution of these intermediates may be obtained from the proposed structures of the labile adducts obtained by addition of acetylenedicarboxylic ester to heterocycles derived from pyridine. These carbide-type intermediates are highly colored; the stable adducts formed from them by suitable treatment are less intensely colored.

Littmann (131) suggests a mechanism for the diene synthesis, which is based on the appearance of the transient yellow color in the α-phellandrene–maleic anhydride reaction and also on the preparation of a polymer of α-phellandrene and maleic anhydride. An intermediate of the type
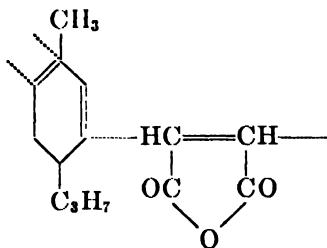
is suggested, wherein there is an alternation of terpene and maleic anhydride molecules. The significance of the dotted lines is not absolutely clear; possibly they indicate a type of coördinate linkage.

B. *The cis principle*

The stereochemical aspects of the diene synthesis have been investigated intensively by Alder and his students. It is a most noteworthy fact that the diene synthesis is highly stereoselective. When several stereoisomers of an adduct are theoretically possible, only one or perhaps two of these isomers are actually formed. These stereochemical phenomena have been discussed and explained in great detail by Alder and Stein in their treatise (27), which will be reviewed at this point. The three-dimensional sketches which appear in the next portions of this review are adaptations from that treatise.

The various stereochemical phenomena attendant on the diene synthesis may be grouped under three main headings. The first of these is the "*cis* principle", which is applicable to all diene syntheses. This principle states that in the diene synthesis, addition of a diene to the dienophilic double bond is invariably a pure *cis*-addition. Accordingly, butadiene and maleic acid give *cis*-1,2,3,6-tetrahydrophthalic acid, and butadiene and fumaric acid give *trans*-1,2,3,6-tetrahydrophthalic acid. A *cis*-dienophile will not give rise to a *trans*-adduct, nor will a *trans*-dienophile give rise to a *cis*-adduct. Fumaric ester will not give *cis*-1,2,3,6-tetrahydrophthalic ester with butadiene. The statement should be qualified to the extent that the *cis*-adduct first formed may isomerize to the *trans*-adduct under the conditions of the experiment, particularly if high temperatures are required to effect addition. Thus while the product actually isolated may apparently be the result of *trans*-addition of the diene to the dienophile, it is postulated that the adduct resulting from *cis*-addition is first formed and that this may isomerize to the product actually isolated.

The cases of butadiene with fumaric and maleic acids are graphically illustrated below:
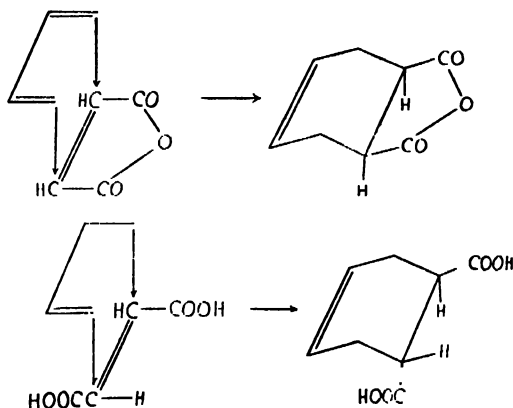
Exclusive of diene addition reactions, there are only a few isolated examples of pure *cis*-additions known. The lecture-hall example is the hydroxylation of double bonds by permanganate. This is practically the sole case of exclusive *cis*-addition known, save for some hydrogenations and the diene synthesis. The hydroxylation by permanganate is illustrated by the formation of meso-

tartaric acid from maleic acid and the formation of racemic tartaric acid from fumaric acid.

C. *The general orientation scheme*

The second heading under which the stereochemical phenomena of diene syntheses may be grouped is termed "the general orientation scheme" by Alder and Stein. The question arising under this heading is whether the diene adds *cis* on one side or the other of the dienophilic double bond. Regardless of which mode of addition actually occurs, the product would be the same if the diene were butadiene, but two isomers are possible with a cyclic diene such as cyclopentadiene. This is illustrated in the two pairs of drawings below. The first pair of drawings represents a side view of the two possible orientations of the reactants. The second pair represents a top view of the two possible orientations, the cyclopentadiene molecule being above the maleic anhydride molecule:
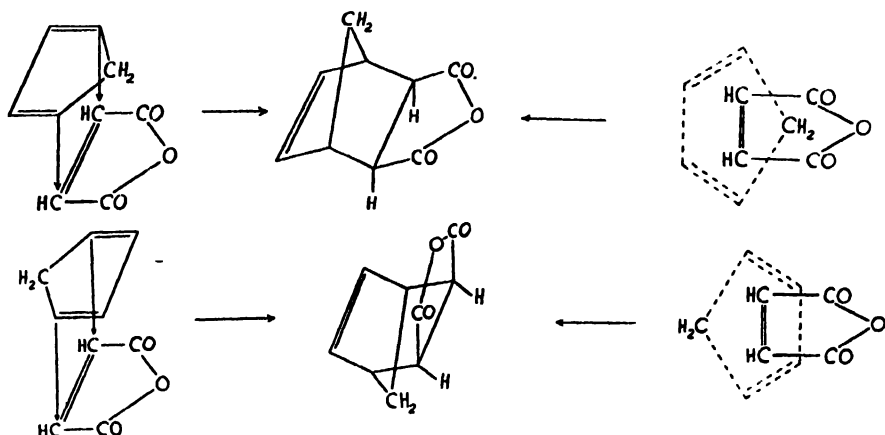
The mode of addition represented by the drawings in which the —CH₂— group of the cyclopentadiene molecule is on the same side of the dienophile molecule as are its carboxylic acid groups gives rise to an acid (I) in which the —CH₂— and carboxyl groups are also on the same side of the molecule. The other two drawings represent a mode of addition wherein the carboxyl and —CH₂— groups are on opposite sides of the double bond of the dienophile; this mode of addition gives rise to an acid (II) in which the endomethylene group is on the opposite side of the molecule from the carboxyl groups. This type of configuration is known as the endo-configuration, whereas the type of configuration possessed by anhydride I is known as the exo-configuration; the prefix "endo" as applied to the —CH₂— bridge should not be confused with the same prefix as applied to the mutual configurations of the carbonyl groups and the bridge itself.

Only one anhydride is formed on the addition of cyclopentadiene to maleic anhydride; this is anhydride II, which is endo-*cis*-1,2,3,6-tetrahydro-3,6-endomethylenephthalic anhydride. Anhydride I, which is not formed in that reaction, is exo-*cis*-1,2,3,6-tetrahydro-3,6-endomethylenephthalic anhydride.

This mode of addition is entirely general; the activating groups which had belonged to the dienophile are always found opposite the endomethylene group with respect to the plane of the six-membered ring (for convenience in discussion, the cyclohexene ring is assumed to be planar). The mode of addition of cyclopentadiene to dienophiles in the absence of complicating factors to be discussed later is exclusively by a mechanism leading to the endo-configuration.
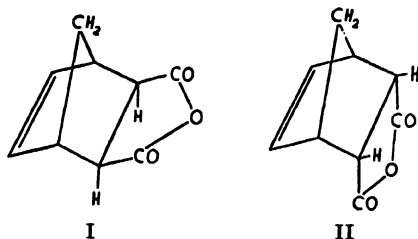
Alder and Stein give a number of proofs of the endo-configuration for the maleic anhydride adduct. One of these rests upon oxidation of the double bond of the adduct. The endo-*cis* adduct was oxidized to the glycol by dilute permanganate; it in turn was oxidized to a cyclopentanetetracarboxylic acid. This acid was found to form a dianhydride. Isomerization of the endo-*cis* acid gave the exo-*cis* isomer. Oxidation of this by the identical procedure used for the endo-*cis* acid eventually yielded a cyclopentanetetracarboxylic acid which formed a monoanhydride, but not a dianhydride:
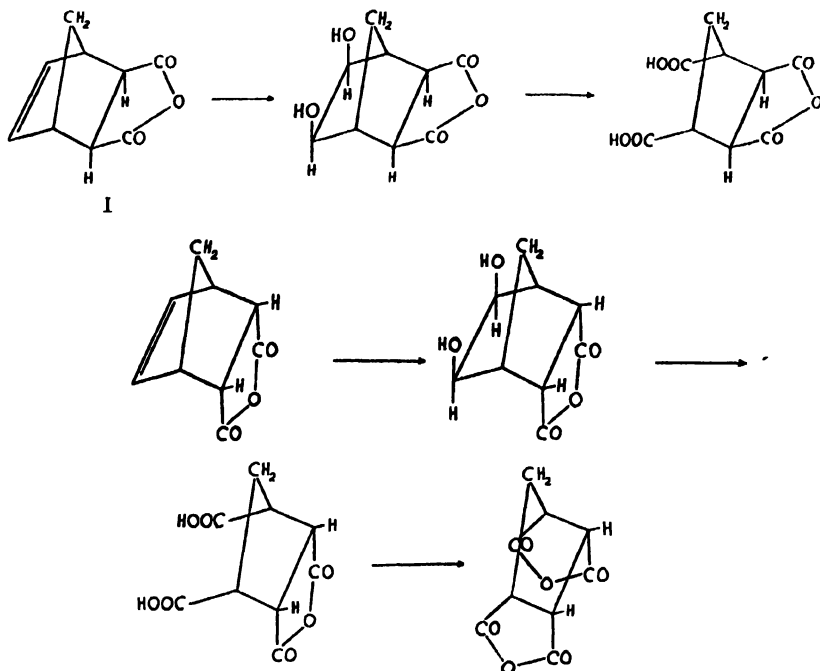
In spite of the fact that cyclopentadiene, cyclohexadiene, and similarly constituted dienes add to give adducts possessing the endo-configuration, it is well not to generalize by stating that all dienes add dienophiles to give adducts possessing the endo-configuration. A better generalization is that dienes add to dienophiles according to an orientation of their molecules which permits maximum accumulation of double bonds just prior to consummation of addition. This statement would include not only the reacting double bonds of the diene and dienophile, but also the double bonds of the carboxyl group and other double bonds of similar character and function. With fulvenes, it also includes the double bond of the C=CR₂ group and double bonds as they may occur in R. In fact, the double bonds of dimethyl- and pentamethylene-fulvenes are so distributed that maximum accumulation of double bonds is slightly in favor of an orientation leading to the formation of the exo-adduct (the adduct is 60 per cent exo-isomer):
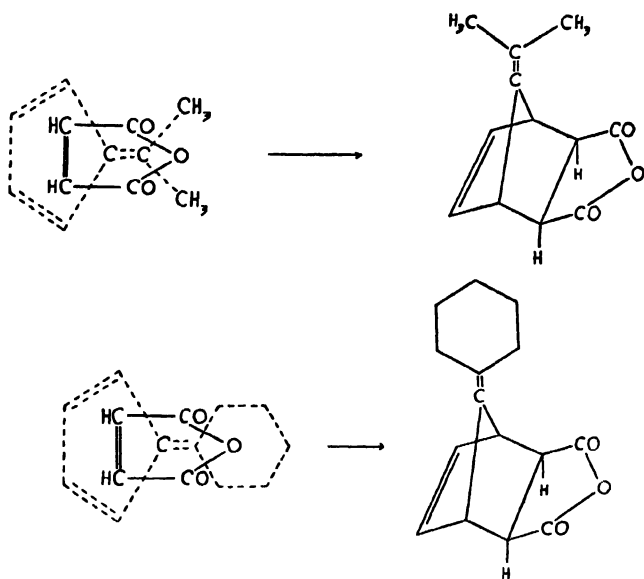
With diphenylfulvene, the double bonds of the phenyl groups are also a determining factor in the orientation of the adduct. In this case, the product is exclusively of the exo-configuration:
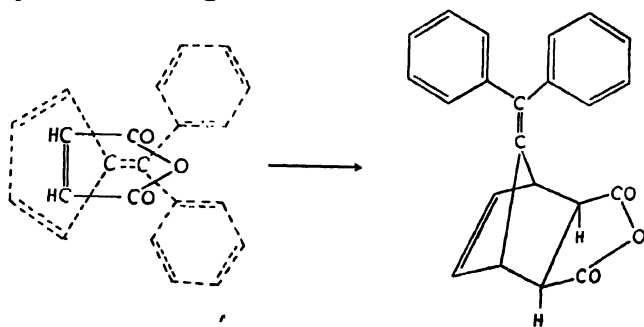
The configuration which would lead to formation of an endo-isomer is the following:
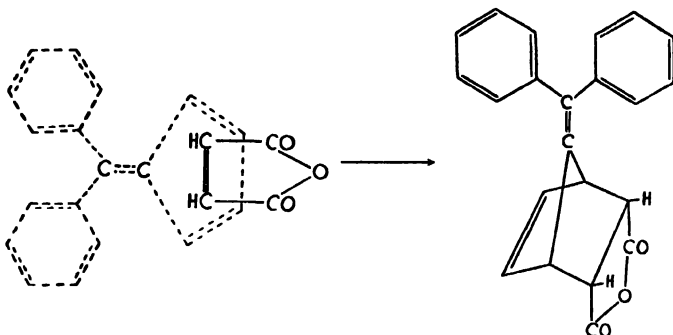
Qualitatively at least, it may be seen that the orientation leading to formation of the exo-isomer permits greater accumulation of double bonds just prior to consummation of addition than does the orientation leading to formation of the endo-isomer.

This rule of maximum accumulation of double bonds applies not only to aliphatic carbonylenic dienophiles, but also to additions to quinones, acetylenic dienophiles, diene dimerizations, etc. Thus, cyclopentadiene dimer is the endo-isomer.

The third heading under which a portion of the stereochemical phenomena of the diene synthesis may be grouped is covered by the question as to whether the diene adds "above" or "below" the dienophilic double bond. The question is of no importance in the majority of diene syntheses, but becomes a factor when additions of dienes to dienophiles such as the adduct of equimolar quantities of cyclopentadiene with an acetylenic dienophile are considered. In general, the question arises when the diene synthesis occurs with a dienophile possessing asymmetric substituents. In the three-dimensional sketch below, the asymmetric centers are marked with asterisks:
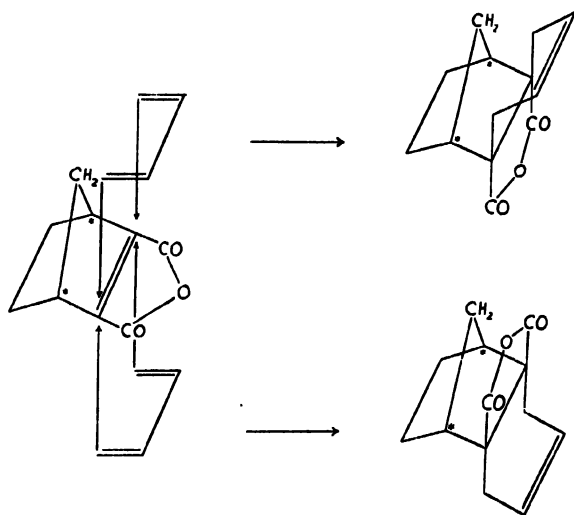
In the case cited, the addition of a diene (such as butadiene) to the adduct of 1 mole of cyclopentadiene to an acetylenic dienophile, the addition proceeds exo with respect to the methylene bridge. This appears to be generally true; while the endomethylene bridge of cyclopentadiene dimer is endo with respect to the activating double bond, further additions of cyclopentadiene to the dimer (which occur at the double bond of the 1:2:2-bicycloheptene ring) resulting in the production of cyclopentadiene trimer, tetramer, etc., result in compounds all of the endomethylene bridges of which are on the same side of the ring system. Hence the dimerization is an endo addition, while further additions are of the exo variety.

Allied to this same type of possible addition are the cases of the bis-diene quinones. *p*-Benzoquinone may add 2 moles of a diene; the addition of the first mole occurs much more rapidly than the addition of the second mole. Since the only rule involved in the determination of structural configuration of the product is the *cis* principle, the bis-diene quinone question may be resolved into a question of the direction of addition of dienes to quinones which have one aliphatic ring fused directly to the *p*-benzoquinone ring, and which have a singly bound pair of fusion atoms. A good example of this is the addition of butadiene to monobutadienequinone (1a,4a,5,8-tetrahydro-1,4-naphthoquinone):
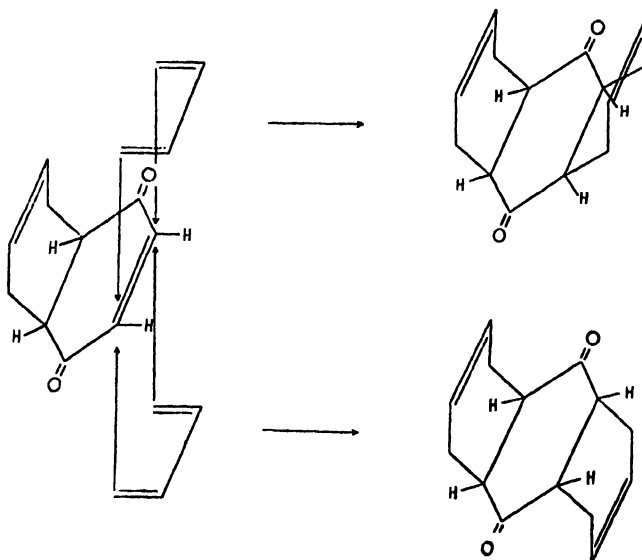
It is known that the bisbutadienequinone (1,4,5,8,1a,4a,5a,8a-octahydro-9,10-anthraquinone) is formed through exclusive *cis*-addition of both molecules of butadiene. This is shown in a number of ways, one being that the reduced quinone (dodecahydroanthraquinone) is oxidizable, giving adipic acid and *cis*-hexahydrophthalic acid without the formation of detectable quantities of the *trans*-isomer. Had both molecules of butadiene added *trans*, or had either one added *trans*, detectable quantities of *trans*-hexahydrophthalic acid would have been formed.

The dodecahydroanthraquinone may be isomerized by alkali or by acetic anhydride to dodecahydroanthraquinone of a different variety. This form would be obtained on reduction of one of the two possible *trans*-addition products of butadiene to *p*-benzoquinone if such actually occurred; oxidation yields adipic and *trans*-hexahydrophthalic acids exclusively. Hence this quinone must be either VI or VII, so no detectable amount of *cis*-hexahydrophthalic acid is found, as would be the case with quinone V.
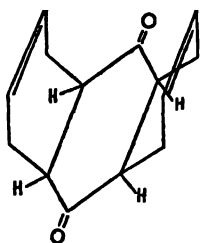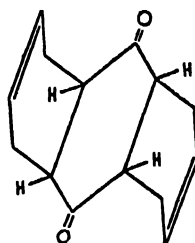
III   IV
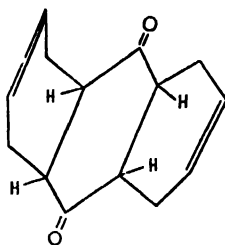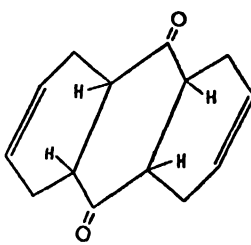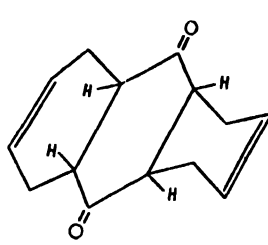
V   VI   VII

Quinone III is of a configuration which would be formed by *cis*-addition of both molecules of butadiene, and the two external rings bear a *cis* relationship to each other. Quinone IV is of a configuration formed in a similar manner, but the external rings are *trans* to each other. Alder and Stein designate these two configurations by the terms, "an-*cis*" and "an-*trans*", respectively. Since both quinones are formed by reduction of *p*-benzoquinonebutadiene in which both molecules of butadiene have added *cis*, III is termed *cis*-,*cis*-,an-*cis*-dodecahydroanthraquinone. Likewise, IV is *cis*-,*cis*-,an-*trans*-dodecahydroanthraquinone. VI is *trans*-,*trans*-,an-*cis*-dodecahydroanthraquinone, and VII is *trans*-,*trans*-,an-*trans*-dodecahydroanthraquinone.

As previously stated, it is known that the bisbutadienequinone formed from *p*-benzoquinone and butadiene is a *cis*-,*cis*-quinone, but it is not known whether it is the an-*cis*- or the an-*trans*-isomer. A guess as to which of these possibilities is actually the case may be based on (*a*) the rule of concentration of double bonds, assuming that the double bond of monobutadiene-*p*-benzoquinone which is in the reduced benzene ring is the deciding factor, and (*b*) on the exo addition of dienes to substances such as 3,6-endomethylene-3,4,5,6-tetrahydrophthalic acid. These considerations lead one to suggest tentatively that the second molecule of butadiene adds exo and that the bisbutadienequinone which is

actually formed is the *cis-*,*cis-*,an-*cis*-isomer, rather than the *cis-*,*cis-*,an-*trans*-form.

Another phase of isomerism and stereochemistry of the diene synthesis which was not discussed by Alder and Stein in their treatise (27) is the formation of one or another or a mixture of isomers when an unsymmetrical diene, such as piperylene, reacts with an unsymmetrical dienophile, such as crotonaldehyde or acrylic acid. In the first place, with acrylic acid one may obtain either tetrahydro-*o*- or tetrahydro-*m*-toluic acid, each of which may be either *cis* or *trans*; the *trans*-isomer may exist in two optically active forms. . No general rule appears to have been stated as to which of the possibilities one may obtain in such additions. Further, no attempt has been made to explain the apparent differences in the reactivity of the *cis*- and *trans*-piperylenes toward maleic anhydride (see page 349). The observation should be checked and the unreactive residue, if any, should be demonstrated to be piperylene or at least a methylbutadiene (see footnote 1).

XVII. DIENANALYSIS

Dienanalysis is, as its name implies, analysis for dienes. The diene number is a quantity defined by Kaufmann and Baltes (257) as $1.269A/W$, where A is the volume in cubic centimeters of tenth-normal alkali which *would have been* necessary to neutralize the maleic anhydride which reacted with W grams of the sample being analyzed. Thus the diene number is a measure of the amount of dienes present in a mixture or, if the diene is pure, it is a measure of the weight per cent of the compound which is in the form of the $C{=}C{-}C{=}C$ group and also a measure of its molecular weight.

The $C{=}C{-}C{=}C$ group itself has a theoretical diene number of 528.75, as do the groups $C{\equiv}C{-}C{=}C$ and $C{\equiv}C{-}C{=}C$. When the first of these last two groups reacts with maleic anhydride, a phthalic acid derivative should be formed, and the reaction ceases with the addition of 1 mole of maleic anhydride. On the other hand, the $C{\equiv}C{-}C{=}C$ group forms a cyclic allene which rearranges to a 1,3-cyclohexadiene. The last named is capable of adding another mole of maleic anhydride; if conditions are such that this may occur quantitatively, the $C{\equiv}C{-}C{=}C$ group will show a diene number of 1057.5, which is much the highest of them all. Accordingly, vinylacetylene is the compound which should have the highest diene number of the simpler compounds (a compound such as octa-1,7-dien-3,5-diyne would have a slightly higher diene number) when it adds 2 moles of maleic anhydride. This number is 976.2. If, on the other hand, conditions are such that only 1 mole of anhydride is added, the observed diene number would be 488.1. Of the compounds which add 1 mole of maleic anhydride only, 1,3-butadiyne has the highest diene number, 507.6. Butadiene has a diene number of 470, which is the highest diene number obtained for all true dienes.

If the diene under consideration will add but 1 mole of maleic anhydride, the diene number will be equal to 25,380 divided by the molecular weight of the diene. If 2 moles are added, then the diene number will be equal to 50,760 divided by the molecular weight.

Kaufmann and Baltes have developed a general method for determination of diene number which is designed particularly for fat analysis, though it may be applied to other compounds with suitable modifications. It consists essentially of heating a 0.1-g. sample of glyceride with excess of a known acetone solution of maleic anhydride for a period of 20 hr., using a sealed tube for the reaction. The excess maleic anhydride is determined by one of two methods: (a) by titration of the filtered aqueous extract of the product with standard alkali, or (b) by addition of an excess of a mixture of potassium iodide and iodate and determination of the iodine formed by thiosulfate titration. Two equivalents of thiosulfate are required per mole of excess anhydride used (257, 260).

Diene numbers have been determined for a number of fats and terpinoid bodies (233, 257, 258, 259, 260, 261, 262). These range from zero for synthetic triolein, palm-kernel oil, and cacao butter to 46.0 for bay oil. Oils such as cottonseed and peanut, which do not contain dienic glycerides as far as is known, also show diene numbers. These numbers are usually quite low, being in the range of 5 to 10, and are provisionally attributed to the presence of dienic substances in the nonsaponifiable fractions. There is also a possibility that the dienic esters which might be present in the original fat undergo alteration on saponification, for the acids obtained by the saponification of such fats do not show diene numbers. The method is more reliable for dienic glycerides than analysis of fats with iodine or thiocyanogen, for these two methods show other unsaturated acids as well as conjugated dienic acids (258, 259).

Accordingly, the iodine and thiocyanogen numbers of the Chinese wood oils indicated about 10 per cent more eleostearic acid than did the diene number. This discrepancy was found to be due to linolic acid and oleic acid. A typical sample gave the following analysis: 74.5 per cent eleostearic acid, 9.7 per cent linolic acid, 8 per cent oleic acid, 3.3 per cent saturated acids, 0.1 per cent unsaponifiable matter, and 4.5 per cent glycerol residues (258). The oil of the pits of the oiticaca tree showed a similar discrepancy between the results obtained by the diene analysis method and those obtained by the iodine or thiocyanogen method (259). Further analysis of a sample showed 70 per cent licanic acid, 15.2 per cent unsaturated nonconjugated acids, 9.9 per cent saturated acids, 0.4 per cent nonsaponifiable matter, and 4.5 per cent glycerol residues.

Dienanalysis has been applied to a limited extent in the petroleum industry. Birch and Scott (91) and Grosse-Oetringhaus (231) studied the quantitative determination of dienic materials in petroleum hydrocarbons, with emphasis on products from cracking and polymerization processes. Grosse-Oetringhaus developed a procedure for the determination which consisted in heating the hydrocarbon mixture with an excess of a solution of maleic anhydride in xylene (the strength of this solution was about 0.2 molar). In order to minimize polymerization and possible reactions between ethylenic hydrocarbons and maleic anhydride, the temperature was not allowed to rise over 100°C. Results were not very consistent, the diene number tending to increase with reaction time, which was varied from 5 to 30 hr. Toluene gave unreliable results.

A gasometric method of analysis of gases containing reactive dienes was developed by Tropsch and Mattox (343), who absorbed the diene in a special

absorption pipet containing molten maleic anhydride. Their method was employed by Robey (309), who analyzed piperylene obtained from cracked gas-oil and also by dehydrochlorination of chloropentanes. Absorption ceased before theoretical amounts were absorbed, and this phenomenon was ascribed to differences in reactivities between the *cis*- and *trans*-forms (see pages 350 and 504).

An obvious application of dienanalysis is the determination of the purity of a sample of diene. A sample of eucalyptus oil was found to contain 18.8 per cent of *l*-α-phellandrene, and increase of the proportion of *l*-α-phellandrene during the process of purification could be followed conveniently by means of dienanalysis. Variation of the length of reaction time made but little difference after the first 2 hr., for a sample of commercial α-phellandrene gave a diene number of 98.0 in a 2-hr. reaction period and a diene number of 99.2 in a 10-hr. reaction period. This corresponded to 53 per cent phellandrene. A commercial myrcene (262) gave a diene number of 134.3 in 30 min. reaction time and a number of 144.1 in 90 min. reaction time. A number of 145.1 was observed after 135 min. reaction time, corresponding to 77.4 per cent pure myrcene. α-Terpinene reacts quantitatively with maleic anhydride at room temperature, and may be estimated and detected.

XVIII. SYNTHETIC AND MISCELLANEOUS APPLICATIONS OF THE DIENE SYNTHESIS

To close this review of the diene synthesis, some of the various applications of the diene synthesis in synthetic and other uses will be shown. A large number of the studies which were reviewed were concerned chiefly with syntheses of certain desired substances, and the diene synthesis was merely a convenient tool with which to achieve these ends.

Polyakova (303, 421) utilized the diene synthesis for the preparation of pure anthracene from coal-tar anthracene. The crude material was heated with over twice the theoretical quantity of maleic anhydride at 140–150°C. for 4 hr. The product was then digested with 10 per cent alkali and filtered. The filtrate was acidified with sulfuric acid, and the adduct was collected, washed, dried, and heated at 300°C. The sublimate, consisting of a mixture of maleic anhydride and anthracene, together with small amounts of re-formed adduct, was extracted with 10 per cent alkali. The residue was anthracene of 95–97 per cent purity. Dermer and King (401) employed a similar method, conducting the distillation of the adduct from soda lime, thereby removing maleic anhydride and preventing re-formation of adduct.

Billing (90) heated crude, gaseous maleic anhydride at 160–200°C. with terpinene, pinene, or rosin, producing resinous products. Resins from rosin and maleic anhydride have been described by Powers (304). The American Cyanamid Co. (53) has used polyterpenes.

Bradley and Johnston (396) state that thermal polymerization of drying oils is largely a Diels–Alder reaction which is preceded by rearrangement of isolated double bonds to a conjugated system. Alekseeva (384, 385) states that the

diene synthesis accounts for a considerable portion of the reactions in the copolymerizations of butadiene with styrene and with methacrylonitrile.

Martin, Gruse, and Lowy (292) studied the effect on gum formation in cracked petroleum distillates after dienes were removed by maleic anhydride.

Pirsch (302) offered circumstantial evidence for Alder and Stein's formulae for the polymers of cyclopentadiene. He employed cyclopentadiene dimer, the dihydro, and the tetrahydro derivatives as solvents for micromolecular-weight determinations. As in the cases of camphor and related substances, the molecular depressions were high in all instances, being 46.2°, 45.4° and 35°, respectively. Pirsch has correlated molecular depressions with structures of various compounds used as solvents which belong to the isocamphane group.

As may have been evident, the various adducts discussed in this review have shown differing degrees of heat stability, which range from the rather highly stable adducts of the simple dienes with maleic anhydride to the adducts of fulvenes and arylated anthracenes which dissociate in solution to their generators in reactions which obey the law of mass action. This variance in adduct stability was made useful in a most ingenious preparation of the acid chloride of acetylenedicarboxylic acid (172). When this acid is treated with phosphorus pentachloride, there is obtained chlorofumaroyl dichloride. The method successfully employed was as follows: The adduct of anthracene with acetylene dicarboxylic acid was treated with phosphorus pentachloride, thus forming the adduct acid dichloride in 33 per cent yield. On heating this acid chloride with maleic anhydride, displacement of dienophile occurred, and the products were the acid chloride of acetylenedicarboxylic acid and the anthracene–maleic anhydride adduct. Some interaction between the products did occur, for there were also formed fumaroyl dichloride and chloropropiolyl chloride. The series of reactions is indicated below:
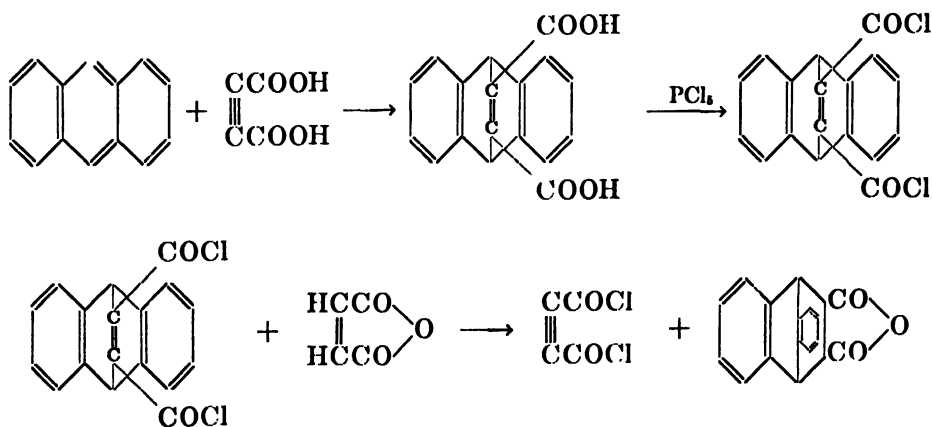
Alder and Windemuth (41, 42) used the diene synthesis in the preparation of bridged hydrocarbons. The first was bicyclo-(1:2:3)-octane, prepared by treatment of the allylamine adduct of cyclopentadiene with nitrous acid, oxida-

tion of the resulting alcohol to the corresponding ketone, and then reduction to the hydrocarbon:
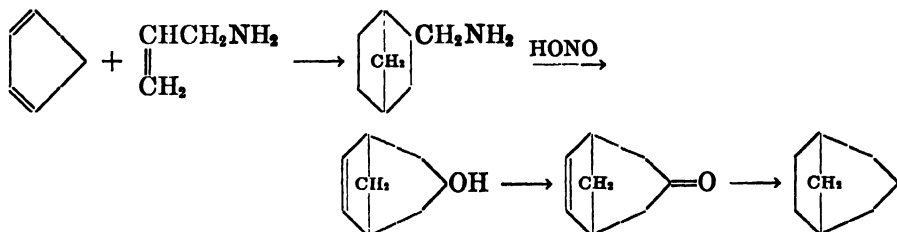
The second synthesis (42) was that of 1,4,5,8-bis(endomethylene)decalin. The acrolein adduct of cyclopentadiene was caused to add a second mole of cyclopentadiene. The resulting aldehyde was reduced and then converted into the enol acetate, oxidation of which gave a cyclic ketone. This ketone was reduced by sodium and alcohol at 200°C. to give the hydrocarbon:
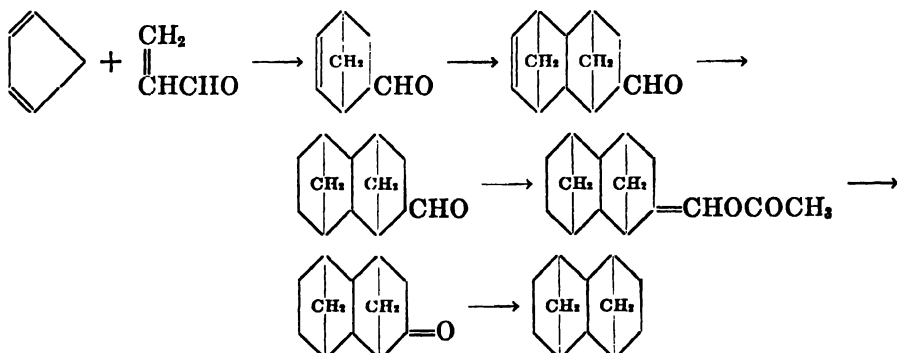
These two hydrocarbons are closely related to the terpinoid bodies. A number of such materials have been synthesized using the diene synthesis in one stage or other of their syntheses. A "pseudo-irone" was prepared by Diels and his students (144) by the reaction of crotonaldehyde with 1,3-dimethylbutadiene, followed by condensation of the adduct with acetone:
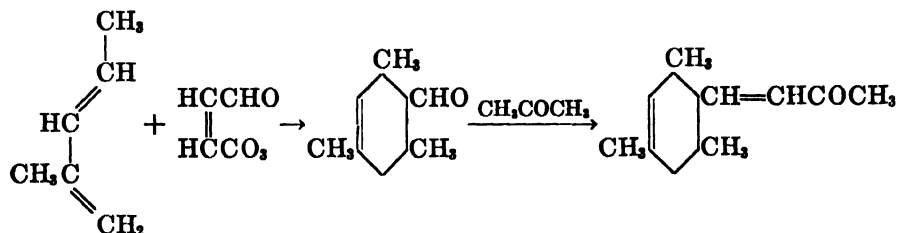
A similar product, containing an additional methyl group, was synthesized by employing 1,1,3-trimethylbutadiene in place of 1,3-dimethylbutadiene:

$$\begin{array}{c}
\text{CH}_3 \\
| \\
\text{CHCH}_3 \\
\text{HC} \\
\parallel \quad + \quad
\begin{array}{c}\text{HCCHO}\\ \parallel \\ \text{HCCH}_3\end{array}
\rightarrow \\
\text{CH}_3\text{C} \\
\parallel \\
\text{CH}_2
\end{array}$$
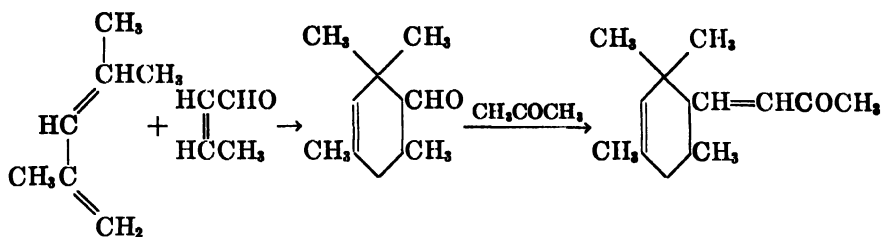
Norcamphor (144, 150) was synthesized by the reaction of acrolein with cyclopentadiene and reduction of the resulting adduct to the fully saturated aldehyde (I). The aldehyde group was eliminated and norcamphor was the end product. There are at least three ways of eliminating the aldehyde group, such as (a) treatment with acetic anhydride and sodium acetate to form the enol acetate, followed by oxidation; (b) treatment with a Grignard reagent, dehydration of the carbinol thus formed, and splitting of the resulting olefin with ozone or some other oxidizing agent; and (c) a roundabout method used by Diels and Alder, which consists in reduction of the saturated aldehyde to the corresponding alcohol, formation of the corresponding iodide by treatment with hydrogen iodide, formation of a quaternary iodide by treatment with trimethylamine, pyrolysis with alkali to yield norcamphene, and finally with ozone to yield norcamphor:

(a) [structure: CHO, CH₂] ⟶ [=CHOOCCH₃, CH₂] ⟶ [=O, CH₂]
I

(b) [structure: CHO, CH₂] → [CHOHCR₃, CH₂] → [=CHCR₃, CH₂] → [=O, CH₂]
I

(c) [structure: CHO, CH₂] ⟶ [CH₂OH, CH₂] ⟶ [CH₂I, CH₂] ⟶
I

[CH₂N(CH₃)₃I, CH₂] ⟶ [CH₂N(CH)₃OH, CH₂] ⟶

[=CH₂, CH₂] ⟶ [=O, CH₂]
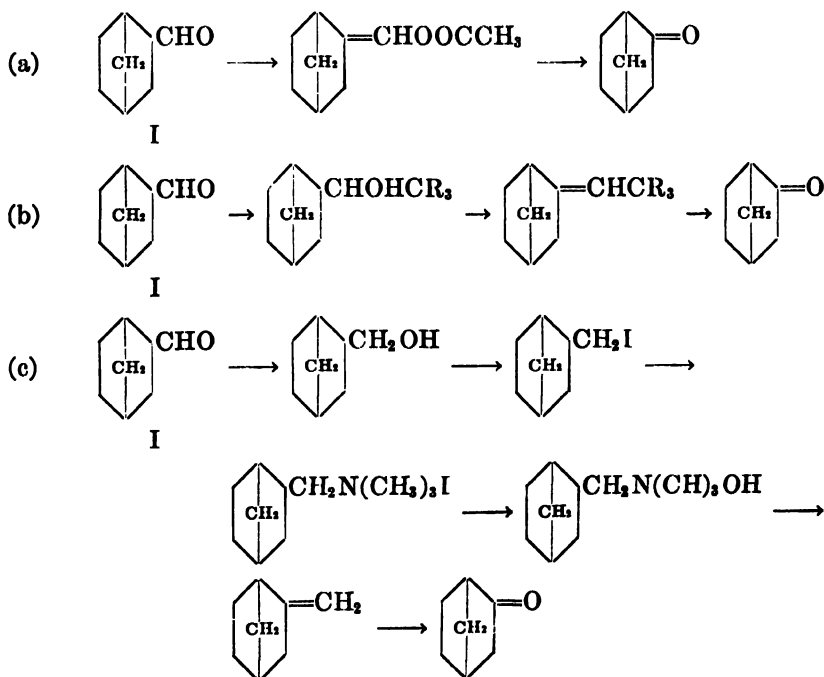
Camphenilone was synthesized from the norcamphor by double treatment with sodium amide and methyl iodide.
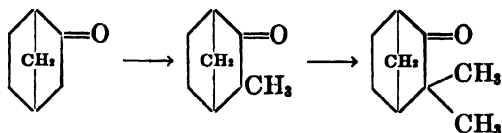
Santene (150) was synthesized by the reaction of cyclopentadiene with crotonaldehyde, and the adduct was reduced to the saturated aldehyde. This was converted into methylnorcamphor by means of acetic anhydride and sodium acetate, followed by ozonization. Methylmagnesium iodide reacted with methylnorcamphor to give γ-santenol, which was dehydrated to santene by heating with potassium sulfate:
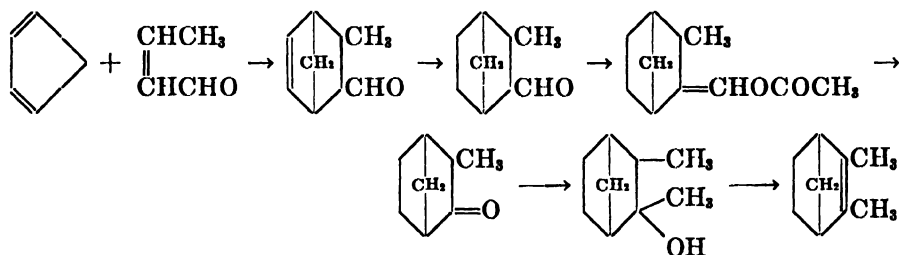
Norborneol (37) was synthesized by reduction of the adduct of cyclopentadiene and acrylic acid to 2,5-endomethylenehexahydrobenzoic acid. This acid was converted into its acid chloride, and thence into the acid azide. The azide was decomposed into norbornylamine by the usual Curtius degradation. The norbornylamine yielded norborneol on treatment with nitrous acid. In a similar fashion, an amino derivative of norbornylamine (1,2-diaminobicyclo-1:2:2-heptane) may be made beginning with the adduct of cyclopentadiene and maleic acid.
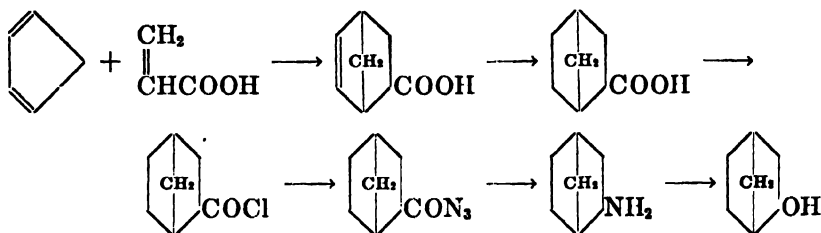
Two terpene preparations, those of dl-limonene and diprene, have been discussed under the heading "Dimerization". A considerable number of other preparations have been either discussed or else mentioned briefly in connection with other diene reactions. In the main, the syntheses presented in this section up to this point have not been discussed in this review in connection with other diene syntheses. From this point on, there will be considered representative synthetic methods employing the diene reaction which have been alluded to previously.

2,5-Dimethylhexa-1,5-dien-3-yne (100), was employed for the synthesis of 1,5-dimethylnaphthalene, as was indicated on pages 380 and 386. The reactions involved in the degradation of the adduct seem rather obvious; they are dehydrogenation and decarboxylation.

Dufraisse and Compagnon (185) synthesized rubrene from α-naphthoquinone and diphenylisobenzofuran; the diene itself was formed by a synthesis involving the diene reaction (this has been rather well covered on page 477).

Fieser, Fieser, and Herschberg (211, 215) have employed the diene synthesis in the preparation of substituted anthraquinones. In general, an aroylacrylic acid was allowed to react with a diene. The adduct was converted into an ester which was dehydrogenated to a 2-aroylbenzoic acid ester. This ester was then cyclized to give the desired anthraquinone. The aroylacrylic acid was prepared by condensation of the appropriate aromatic hydrocarbon with maleic anhydride, using aluminum chloride as the condensing agent. Unless both the diene and aroylacrylic acid were symmetrically substituted, or unless the aroylacrylic acid had one of its ortho-positions blocked if unsymmetrically substituted, uncertainty as to the structure of the resulting quinone will arise. This may be illustrated by (a) the reactions of p-toluylacrylic acid with 2,3-dimethylbutadiene, (b) the reactions of p-toluylacrylic acid with piperylene, (c) the reactions of m-toluylacrylic acid with 2,3-dimethylbutadiene, and (d) the reactions of 2,4-dimethylbenzoylacrylic acid with butadiene:

(a)
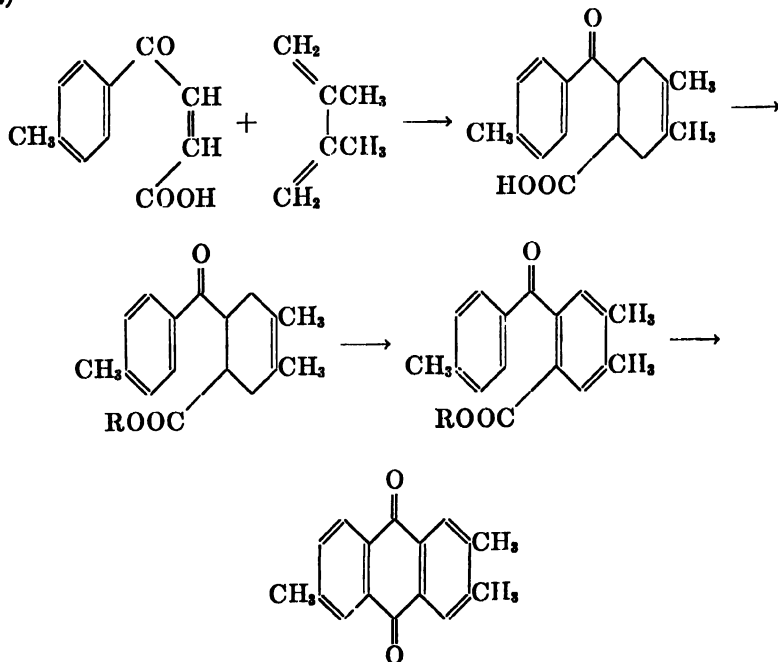
(b)
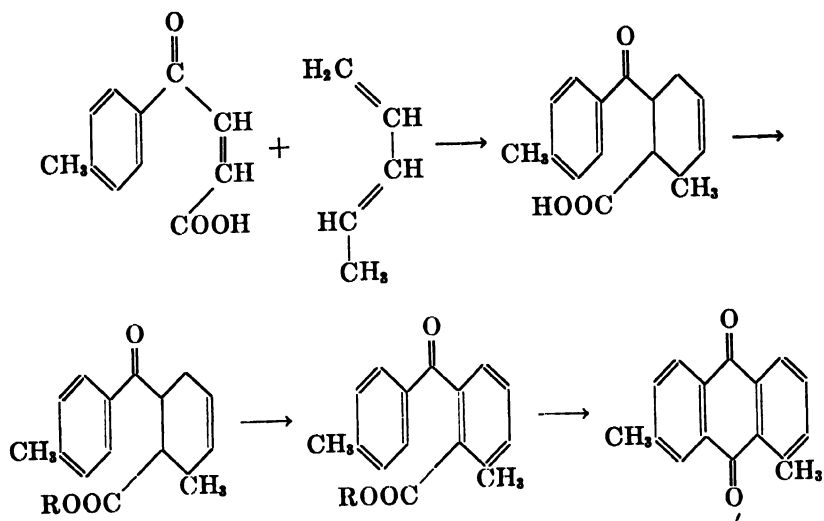
or
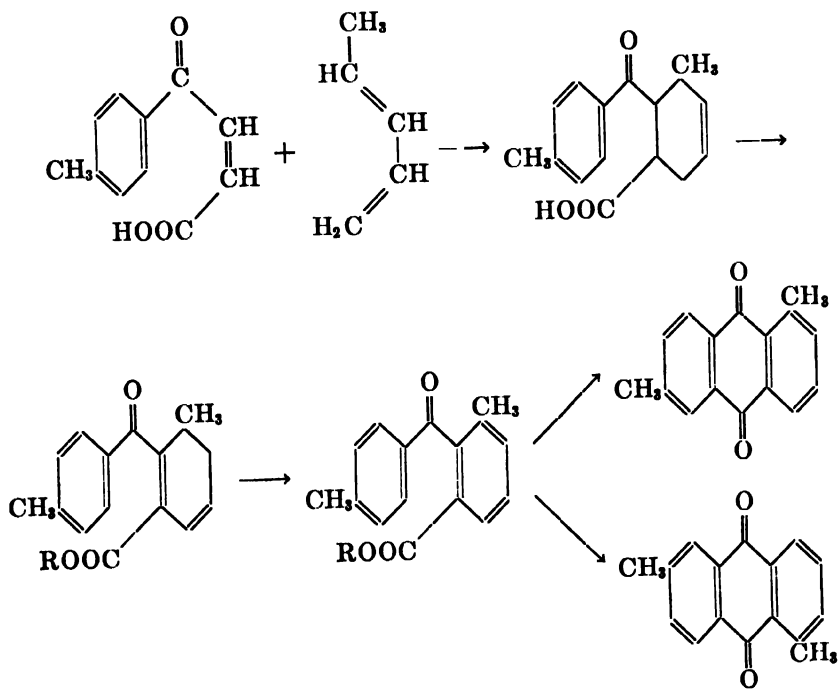
(c)
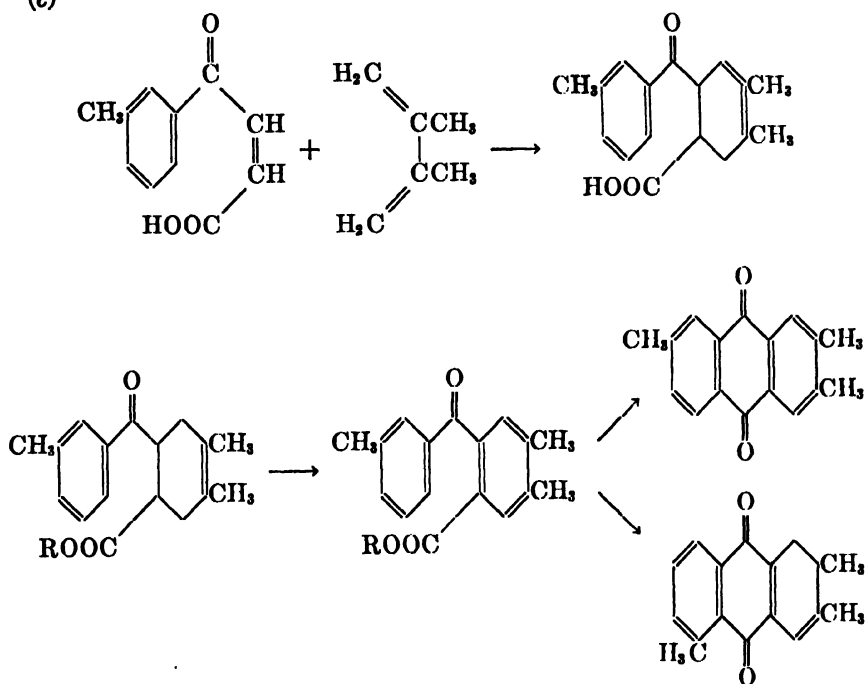
(d)
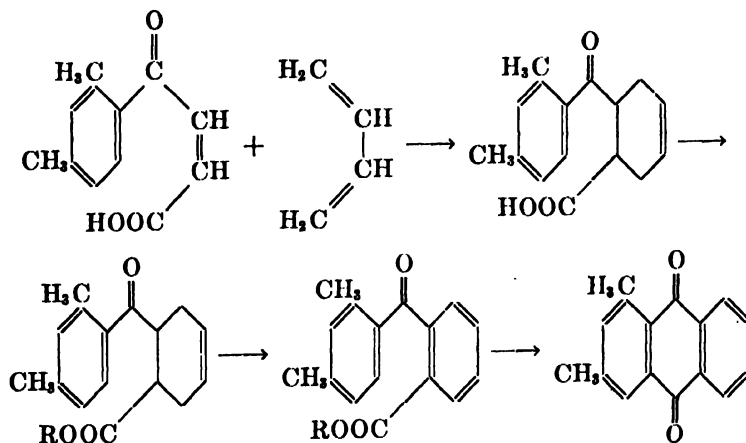
Certain of the above instances have been discussed by Fieser, Fieser, and Herschberg (213); those which they did not discuss are examples selected by the author of this review in order to show the possibilities of production of isomeric substances.

Fieser and Herschberg (213) synthesized chrysene by a series of reactions which involve the diene synthesis as one of the steps:
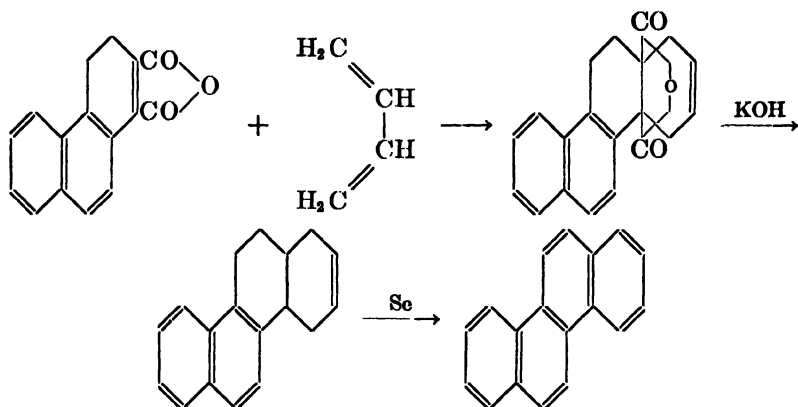
It may be seen that this method is perfectly general, for by use of the appropriate diene any desired chrysene possessing substituents in one of the external rings may be synthesized.

Substituted biphenyls may be produced from 1-phenylbutadiene via the diene synthesis:
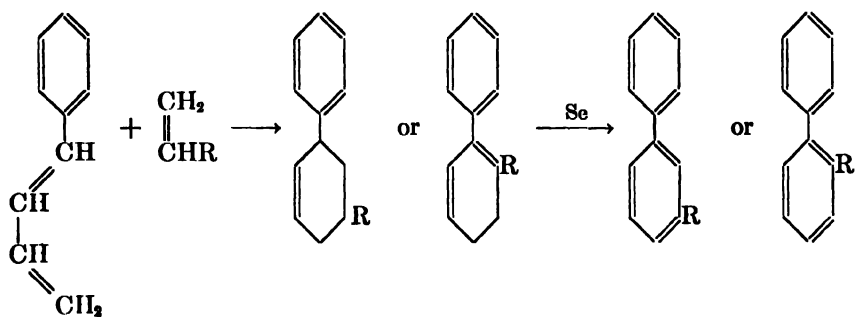
Substituted anthraquinones may be obtained by a more direct method than that used by Fieser. α-Naphthoquinone may be caused to react with suitably substituted butadienes or cyclohexadienes. The adduct is heated in air, whereupon oxidation occurs (the adduct with cyclohexadiene will split out olefin simultaneously) and a substituted anthraquinone is obtained.
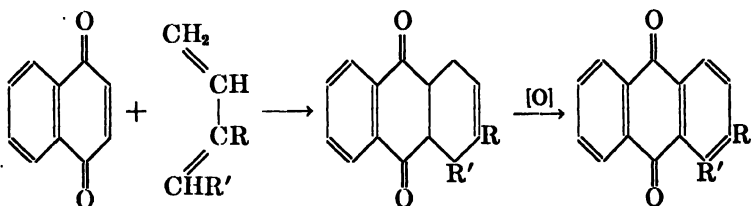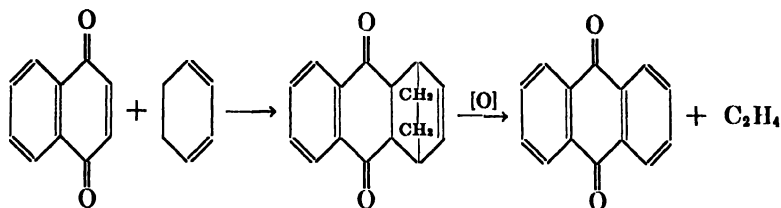
Fieser and Novello (406) have prepared 4,10-ace-1,2-benzanthracene, starting with 1,2,3,6-tetrahydrophthalic anhydride.

The valuable aid of Mr. Angelo J. Longo in furnishing a number of references which had been overlooked by the author and in proofreading the manuscript and galleys is hereby gratefully acknowledged.

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LIQUID AMMONIA RESEARCH—1941

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CONTENTS

I. INTRODUCTION

Attention is called to the fact that this paper represents a continuation of the review series initiated in 1933 and heretofore published in the *Journal of Chemical Education* (20, 22, 84, 85, 87, 90, 93, 94). In this and in subsequent reviews, it will be the authors' purpose to present annually a brief concise account of researches involving liquid ammonia, a solvent and reaction medium which in recent years has passed from the realm of the chemical curiosities into the category of common and useful laboratory tools. The extent to which liquid ammonia has come into general use is amply illustrated by the character and variety of the applications cited in the following pages.

II. PHYSICOCHEMICAL STUDIES

Measurement of the conductance of liquid ammonia solutions of benzamide, o-, m-, and p-toluamides, o-, m-, and p-tolusulfonamides, o-, m-, and p-chlorobenzamides, o- and m-bromobenzamides, and their sodium or potassium salts has been made for the purpose of determining the relationship between the position of substitution and the magnitude of the ionization constant (57). In general, methyl substitution resulted in a decrease in the ionization constant. In the case of the substituted benzamides, the relative magnitudes of the effects produced are given by the order: para > meta > ortho. With benzenesulfonamide, meta and para substitution decreased the value of the ionization constant to about one-half that of the unsubstituted compound, while ortho substitution produced only a slight decrease.

The mean activity of potassium iodate corresponding to infinite dilution has

been determined for liquid ammonia solutions at 25°C. by measuring the solubility of this salt in the presence of electrolytes at different ionic strengths and extrapolating to zero ionic strength (2). The electrolytes used were sodium chloride, potassium chloride, potassium bromide, potassium iodide, and ammonium chloride. The results failed to conform to the Debye–Hückel limiting law. The observed deviations have been attributed to the fact that the lower dielectric constant of ammonia (relative to water) causes the electrostatic forces between ions to become the predominating factor. The molar heats of solution of ammonium iodide, sodium iodide, sodium chloride, sodium nitrate, and methanol in liquid ammonia have been measured by Schmidt and coworkers (69). In contrast to ammonium chloride and ammonium bromide, which were studied earlier (23), ammonium iodide was found to have a negative heat of dilution.

Ecker (31) has described studies on the absorption spectra of saturated liquid ammonia solutions (−50°C.) of reversible polymers obtained from certain quinoline dyes. Aqueous solutions of diethyl-ψ-isocyanine exhibit an absorption band at 20,750 cm.$^{-1}$ which is attributed to the presence of a dimer. Absence of this band in the spectrum of the corresponding liquid ammonia solution suggests that the dimeric form is absent, probably because the solubility of the dye is too low to permit polymerization.

The ammonolysis of 2-chlorobenzothiazole by liquid ammonia at 20° and 30°C. has been found to be a pseudo-unimolecular reaction which is not appreciably catalyzed by relatively high concentrations of salts (55). Those salts which behave as acids in liquid ammonia failed to exhibit the catalytic activity which might be anticipated, in view of the pronounced effects which such salts are known to have upon the ammonolysis of esters. The most probable reaction mechanism has been shown to be a bimolecular interaction of molecules of the thiazole and molecules of ammonia. Reaction-velocity constants and the energy of activation for the reaction have been calculated from the experimental data.

A spongy porous suspension of calcium metal in toluene has been prepared by Bergstrom and Carson (5) by adding a liquid ammonia solution of the metal to a large volume of toluene, followed by volatilization of the ammonia. As a catalyst for the hydrogenation of naphthalene, the calcium suspension so prepared exhibited essentially the same activity as calcium activated by pulverization under benzene in a ball mill.

In a study of the liquid–gas equilibrium for the system ammonia–nitrogen at pressures up to 5600 kg. per cm.^{2} and over a temperature range of 90–125°C., a temperature minimum between 85° and 90°C. has been observed in the critical temperature–pressure diagram (52). It was found that the composition at the critical point (53 to 57 volume per cent) varied only slightly with the temperatures to which the system was subjected. The original discussion of these results devotes considerable attention to the possible existence of a "barotropic phenomenon" in this particular two-component system. Nomographs for the solubilities of nitrogen and hydrogen in liquid ammonia have been devised (29).

III. INORGANIC REACTIONS

The reducing action of liquid ammonia solutions of sodium, potassium, and calcium toward several soluble and insoluble salts of nickel at $-33.5°C$. has been investigated by Burgess and Eastes (15). The finely divided elemental nickel produced in these reactions was found to be pyrophoric and to be an excellent catalyst for the conversion of the alkali and alkaline-earth metals to the corresponding amides. An appreciable quantity of the hydrogen liberated during amide formation was found to be absorbed by the finely divided nickel. However, upon being heated above $360°C$. *in vacuo*, the absorbed hydrogen was liberated and the metal lost its pyrophoric properties. The elemental nickel produced by reduction with calcium was found to be more active than that formed when either sodium or potassium was employed, a behavior which has been observed previously (88) in a study of the reduction of silver iodide. The preparation of $K_4Ni(CN)_4$ by Burgess (14) and of $K_4Pd(CN)_4$ by Fernelius (33) has been referred to by Blanchard (7) in connection with a discussion of metal carbonyls. These unusual substances were prepared by treating solutions of potassium nickelocyanide, $K_2Ni(CN)_4$, and potassium palladocyanide, $K_2Pd(CN)_4$, respectively, in liquid ammonia with potassium. Further discussion of these interesting compounds will be deferred until additional details are published.

The reaction between arsine and lithium in liquid ammonia (54) at $-70°C$. has been shown to proceed in accordance with the equation:

$$AsH_3 + Li + xNH_3 \rightarrow LiAsH_2 \cdot 4NH_3 + \tfrac{1}{2}H_2 + (x - 4)NH_3$$

The tetraammonate of lithium dihydrogen arsenide undergoes a two-stage decomposition *in vacuo* at $0°C$., as follows:

$$LiAsH_2 \cdot 4NH_3 \rightleftharpoons LiAsH_2 \cdot 2NH_3 + 2NH_3$$

and

$$2LiAsH_2 \cdot 2NH_3 \rightarrow Li_2AsH + AsH_3 + 2NH_3$$

Dilithium hydrogen phosphide, Li_2PH, has been found to form a white crystalline pentaammonate, $Li_2PH \cdot 5NH_3$, which is only slightly soluble in liquid ammonia and which, *in vacuo*, loses ammonia to form successively a tri- and a di-ammonate (53).

A recent study (37) of the reduction of aryl-substituted bismuth halogenides by solutions of alkali and alkaline-earth metals in liquid ammonia at its boiling point has shown that these reactions may be represented by the equations

$$R_2BiX + M \rightarrow R_2Bi + MX$$

and

$$R_2Bi + M \rightarrow R_2BiM$$
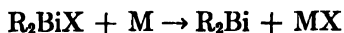
where R represents an aryl substituent, M represents an alkali metal, and X represents a halogen. The metal salts in liquid ammonia solution react with compounds of the type $R'X$ as shown by the equation

$$R_2BiM + R'X \rightarrow R_2R'Bi + MX$$
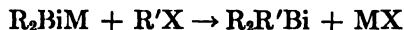
The order of relative stability of diarylbismuth halides is $R_2BiI > R_2BiBr > R_2BiCl$, while for the corresponding R_3BiX_2 types the order is $R_3BiCl_2 > R_3BiBr_2 > R_3BiI_2$.

The preparation, properties, and certain reactions of the amides of tervalent chromium and cobalt have been described by Schmitz-Dumont (70). A red polymeric amide corresponding to the formula $[Cr(NH_2)_3]_n$ was produced by the reaction between the hexammine of chromium(III) nitrate and potassium amide in liquid ammonia at room temperature. The amphoteric character of this amide was shown by the fact that it reacts with ammonium bromide in liquid ammonia to form the complex salt $[(NH_3)_3Cr(NH_2)Br]_nBr_n$, and by the fact that the ammonia-insoluble polymeric amide is dissolved by an excess of potassium amide with formation of the salt $[Cr(NH_2)_4]_nK_n$. An analogous amido-imido potassium salt, $[(HN)Cr(NH_2)_2]_nK_n$, was also formed by treatment of the hexammine of chromium(III) iodide with an excess of potassium amide in liquid ammonia. Similarly, a brown amorphous polymeric amide of cobalt, $[Co(NH_2)_3]_n$, was formed by treatment of the hexammine of cobalt(III) nitrate with potassium amide. That this amide is also amphoteric was demonstrated by the formation of the nitrido salt, $Co_2N_3K_3$, by reaction with excess potassium amide and by the formation of $[(NH_2)Co(NH_3)_2]_n(NO_3)_n$ by reaction with ammonium nitrate in liquid ammonia.

Audrieth and Toy (3) have recommended the use of liquid ammonia for the preparation of phenyl diamidophosphate and diphenylamidophosphate by the ammonolysis of the corresponding phenyl-substituted phosphoryl chlorides.

$$C_6H_5OPOCl_2 + 4NH_3 \rightarrow C_6H_5OPO(NH_2)_2 + 2NH_4Cl$$

$$(C_6H_5O)_2POCl + 2NH_3 \rightarrow (C_6H_5O)_2PO(NH_2) + NH_4Cl$$
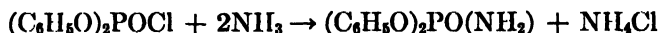
This procedure is characterized by its convenience and by relatively high yields.

The extraction of water from a number of silicate minerals and hydrated oxides by liquid ammonia at $-77°C$. has been described (6). The residues contained both water and ammonia in varying ratios which approached the proportions $2H_2O:4NH_3:6SiO_2$ for minerals of low base content. Minerals of high base content formed gels and the ammonia content followed typical adsorption curves. Adsorption of ammonia was also observed with certain hydrous oxides (CuO, ZnO, La_2O_3, Fe_2O_3, Ta_2O_5), while but little adsorption was exhibited by such hydrated oxides as Na_2O, BeO, CaO, and BaO. Of the hydrous oxides studied, the metal oxides in general formed no definite compounds with ammonia except in the cases of bauxite and hydrargillite, which gave mixed hydrate-ammonates. The more acidic oxides tended toward the formation of ammonates or mixed hydrate-ammonates, e.g., $Cb_2O_5·2H_2O·NH_3$, $Sb_2O_5·5H_2O·3NH_3$, and $H_2WO_4·2NH_3$. The formation of a considerable number of ammonates of complex salts of zinc(II) chloride, cadmium(II) chloride, cobalt(II) chloride, and nickel(II) chloride has been reported (75). These salts in chemical combination with benzidine, o-tolidine, and o-dianisidine were treated with liquid ammonia

and the existence of ammonates was shown by tensimetric measurements. For example, $Cd(Bzd)Cl_2$ was found to form ammonates containing 12, 10, 8, 6, 4, 2, and 1 NH_3. The extent of ammonation, as well as the thermal stability of the ammonates, appear to increase with increase in the atomic volume of the central metal atom. The heats of formation of some seventy-six ammonates have been calculated.

Roberts (66) has called attention to the already generally known fact that no explosion hazard is involved in the use of mercury in contact with liquid or gaseous ammonia enclosed in glass containers.

IV. ORGANIC REACTIONS

A. Ammonolysis

An investigation of the ammonolysis of the α-halogen acids,—α-bromoacetic, α-bromopropionic, α-bromobutyric, α-bromovaleric, and α-bromoisovaleric,— by liquid ammonia at 25°C. has shown that the formation of secondary and tertiary ammonolysis products is markedly inhibited by the presence of ammonium salts (27, 73). This behavior has been attributed to the fact that a relatively high concentration of ammonium ion may favor the reaction

$$H_2NCHRCOO^- + NH_4^+ \rightarrow H_3N^+CHRCOO^- + NH_3$$
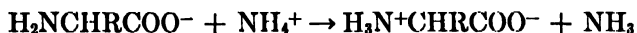
which is strictly analogous to the reaction in aqueous ammonia in which the pH influences the formation of the zwitter ion, $H_3N^+CHRCOO^-$, in a similar reaction.

$$H_2NCHRCOO^- + H_3O^+ \rightarrow H_3N^+CHRCOO^- + H_2O$$
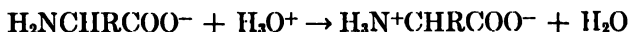
In both cases, the solvated proton is believed to shield effectively the pair of electrons of the nitrogen atom. Comparative studies were made on the yield of glycine obtained using various ratios of ammonia to chloroacetic acid for both liquid and aqueous ammonia. At −33.5°C., chloroacetic acid is not appreciably ammonolyzed by liquid ammonia over a period of 24 hr., while at 30°C. nearly complete ammonolysis was accomplished in about 5 hr. and only 1 hr. was required for complete ammonolysis at 60°C. It was further shown that the longer chain acids were ammonolyzed most readily, and it was concluded that liquid ammonia is an excellent ammonolyzing medium for the less reactive α-halogenated acids of high molecular weight.

3-Methoxymesitamide has been prepared by the interaction of the corresponding acid chloride with liquid ammonia at its boiling point (35).
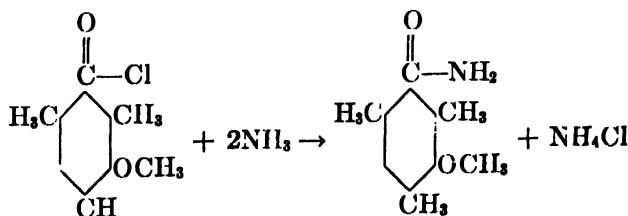
The reaction between bis(chloroacetyl)piperazine and liquid ammonia (56) has been shown to result in the formation of glycinamide and diketopiperazine.

The diamide of norcamphoric acid has been formed by the ammonolysis (by liquid ammonia) of the corresponding dimethyl ester (28). A detailed procedure for the preparation of appreciable quantities of lactamide in 70 per cent yield by the ammonolysis of ethyl lactate by liquid ammonia at room temperature has been described (50). By reaction with liquid ammonia at its boiling point, racemic α-hydroxy-β,β-dimethyl-γ-butyrolactone has been converted to racemic α,γ-dihydroxy-β,β-dimethylbutyramide (62). Starting with the corresponding (−)-lactone, (+)-α,γ-dihydroxy-β,β-dimethylbutyramide was prepared in a similar manner. At 25°C. also, the (−)-lactone is converted quantitatively to the (+)-amide (38).

B. Reactions of alkali amides

The behavior of certain *syn-* and *anti*-aldoximes and their derivatives toward potassium amide in liquid ammonia solutions has been described by Vermillion and Hauser (83). At room temperature, potassium amide and *anti*-4-methoxy-benzaldoxime have been found to yield both the amidine and the corresponding amide by a reaction which is believed to be represented by the equation

$$\begin{array}{c} R{-}C{-}H \\ \parallel \\ HO{-}\ddot{N} \end{array} \xrightarrow{\text{KNH}_2} RCN \xrightarrow{\text{KNH}_2} RC(={NK})NH_2$$
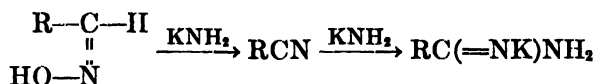
At −33.5°C., potassium amide reacts with *syn-* and *anti*-4-methoxybenzal-doxime O-methyl ethers to form quantitative yields of 4-methoxybenzonitrile. Under similar conditions, *syn-* and *anti*-benzaldoxime acetates yield the corresponding *syn-* and *anti*-aldoximes. It has been shown that either cyclopentadiene or 1,4-pentadiene reacts with sodium amide in liquid ammonia to form a sodium salt (80). The action of sodium amide does not result in any rearrangement of the double bonds in the 1,4-diene. The reaction between sodium amide and alkyl bromides or chlorides in liquid ammonia at −50°C. has been shown to result in the formation of olefins and amines (72). Yields of amines of from 30 to 74 per cent of theory were obtained, using alkyl bromides of from four to twelve carbon atoms. Amines were formed only from halides having the halogen in the primary position, and the alkyl chlorides were found to exhibit a much slower reaction rate than the bromides and resulted in poorer yields of amines. The preparation of the monoamine of cellulose in 74 per cent yield by the interaction of cellulose nitrate and sodium amide, potassium amide, or sodium in liquid ammonia has been reported (68). Strain (77) has observed that carotenes react with potassium amide in liquid ammonia to form products having deep blue colors,

C. Reactions of solutions of metals

1. Alkylation: Audrieth and coworkers (4) have shown that phenylhydrazine reacts readily with alkali metals and alkali amides in liquid ammonia at its boiling point to form metal salts,

$$C_6H_5NHNH_2 + Na \rightarrow C_6H_5N(Na)NH_2 + \tfrac{1}{2}H_2$$

$$C_6H_5NHNH_2 + NaNH_2 \rightarrow C_6H_5N(Na)NH_2 + NH_3$$
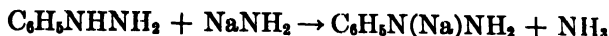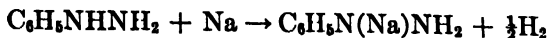
which react with alkyl halides to form unsymmetrical disubstituted α-alkyl arylhydrazines. An excess of sodium was found to cleave the N—N bond in primary and unsymmetrical disubstituted hydrazines.

An application of the methylation procedure, involving treatment with sodium in liquid ammonia at its boiling point followed by addition of methyl iodide (91), to the methylation of cornstarch and certain dextrins has been described (16). Using a similar procedure, Hassid, Joslyn, and McCready (41) have methylated an insoluble polysaccharide isolated from yeast. These workers imply an element of novelty in their use of anisole as a diluent. Actually, the use of such diluents in the alkylation procedure was first suggested by Muskat (86) and the use of anisole specifically has been described in detail by Hess and Lung (89).

2. Reactions of alkali acetylides: The reduction of dialkylacetylenes by sodium in liquid ammonia at its boiling point has been shown to lead, almost exclusively, to the formation of pure *trans*-olefins in good yields. By this method, the *trans* isomers of 3-hexene, 3-octene, 4-octene, 5-decene (18), 2-hexene, and 2-octene (19) have been prepared. The apparent general applicability and unidirectional character of these reactions, together with the fact that the corresponding *cis* isomers may be prepared by catalytic hydrogenation in the presence of Raney nickel, suggest that these methods will come to occupy a position of considerable importance among methods of olefin synthesis. Reduction by sodium in liquid ammonia has also been extended to the preparation of 1-alkenes from the monoalkylacetylenes, and two acetylenic carbinols have been reduced similarly.

A study of the use of lithium acetylide in the preparation of amylacetylene (from $LiC\equiv CH$ and $n\text{-}C_5H_{11}Br$) and methylethylethynylcarbinol (from $LiC\equiv CH$ and $C_2H_5COCH_3$) in liquid ammonia at its boiling point (17) has shown that the yields obtained are comparable to those resulting from the use of sodium acetylide. Contrary to an earlier report, it is claimed that freshly prepared lithium acetylide does not contain lithium carbide but that, during isolation from liquid ammonia solutions, the acetylide decomposes to form an approximately equimolar mixture of acetylide and carbide. Lithium amylacetylide (from $n\text{-}C_5H_{11}C\equiv CH$ and $LiNH_2$ in liquid ammonia), on the other hand, was found to be stable both in ammonia and in the solid state. In connection with the preparation of 3-methyl-1-butyn-3-ol by the reaction between acetone and sodium acetylide in liquid ammonia, Taylor and Shenk (81) have found that the concurrent formation of 2,5-dimethyl-3-hexyn-2,5-diol is promoted by slow evaporation of the liquid ammonia and aging of the reaction mixture prior to hydrolysis. It had been shown previously (92; *cf.* 34) that diol formation may be suppressed by conducting the condensation of acetone and sodium acetylide at $-50°C$. in the presence of an excess of acetylene.

A recently developed method for the preparation of α-acetylenic acids may be summarized by the following equations (97):

$$HC\equiv CH + Na \rightarrow NaC\equiv CH + \tfrac{1}{2}H_2$$

$$NaC\equiv CH + RBr \rightarrow RC\equiv CH + NaBr$$

$$RC\equiv CH + NaNH_2 \rightarrow RC\equiv CNa + NH_3$$

$$RC\equiv CNa + CO_2 \rightarrow RC\equiv CCOONa$$

$$RC\equiv CCOONa + NaHSO_4 \rightarrow RC\equiv CCOOH + Na_2SO_4$$
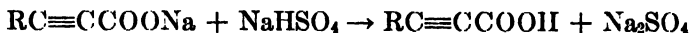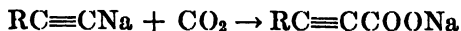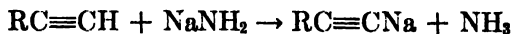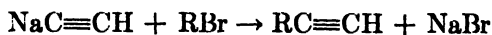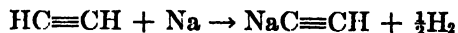
The first three of the reactions indicated above were carried out consecutively in liquid ammonia solutions at temperatures below the boiling point. Carbonation and acidification were conducted in the presence of an inert diluent after removal of the solvent ammonia. By this procedure, ethyl-, propyl-, butyl-, and amyl-propiolic acids were prepared.

3. Other reduction reactions: Further observations on the reduction of terphenyl by sodium in liquid ammonia (47) have shown that, in addition to dihydroterphenyl, there is also formed a hydrocarbon product in quantities which increase with increase in the quantity of sodium employed. The dihydroterphenyl, however, is not further hydrogenated by using an excess of sodium over and above that required for the formation of the dihydro derivative. Stoelzel (76) has reported that triphenylamine is unreactive toward solutions of sodium in liquid ammonia at $-75°C$. over periods up to 24 hr. Indole has been prepared in 50 per cent yield by the intramolecular condensation of o-formotoluide, using potassium or potassium amide in liquid ammonia as the condensation agent (82). Sodium amide was found to be unsatisfactory.

Brown and du Vigneaud (11) have prepared S-(β-amino-β-carboxyethyl)homocysteine by the reaction of methyl α-amino-β-chloropropionate hydrochloride with homocysteine, which was obtained by the reduction of S-benzylhomocysteine by sodium in liquid ammonia at its boiling point (21). Mesolanthionine (β-amino-β-carboxyethylsulfide) has been synthesized in a similar manner by the interaction of l-cysteine and methyl dl-α-amino-β-chloropropionate hydrochloride (30). The d-, l-, and dl-forms of lanthionine have also been prepared (12). Carter and coworkers (26) have reported the removal of the benzyl group from α-amino-β-benzylthiobutyric acid by reduction with sodium in liquid ammonia (21). The acid so obtained was treated with sodium in liquid ammonia, followed by addition of benzyl chloride to produce the original benzyl derivative. By means of a procedure described previously (24), asparthione (β-aspartylcysteinylglycine) has been prepared in 70 per cent yield by the reduction of carbobenzoxy-β-aspartyl-S-benzylcysteinylglycine (60). Sodium in liquid ammonia was employed as the reducing agent. The reduction product was isolated as its mercury and copper salts and finally as the tripeptide. Cystine has been prepared by the reduction (by sodium in liquid ammonia) of S-benzylcysteine resulting from the hydrolysis of the product obtained by treating silk with benzyl mercaptan in the presence of alkali (61). Brown and du Vigneaud (13) have reported that the physiological activity of biotin is not destroyed by exposure to the strong reducing action of sodium dissolved in liquid ammonia.

Applications of the liquid ammonia–sodium method for the determination of

total halogen in organic combination (59) to the analysis of β-dimethylamino-
ethyl bromide hydrobromide (1) and of products obtained by the interaction
of toluene and chlorine (49) have been reported.

D. Other organic reactions

The report (36) that β-phenethylamine may be prepared in from 80 to 90 per
cent yields by the catalytic hydrogenation of benzyl cyanide has been confirmed
(25). The hydrogenation was carried out using liquid ammonia as the solvent
and a Raney nickel catalyst. Crude glycerol, produced by the hydrogenolysis
of dextrose, has been purified by crystallization from liquid ammonia (40; cf. 39).
Crystallization was completed within 30 min. after seeding a 1:1 mixture of gly-
cerol and liquid ammonia at −33.5°C.

Roberts and coworkers (67) have reported qualitative studies on the behavior
of curare toward liquid ammonia at its boiling point and toward glycine in liquid
ammonia. All of the products so obtained were found to be biologically active.
Treatment of a number of polysaccharides with liquid ammonia has been shown
to result in changes in optical rotation but only slight alterations in anti-
genicity (32).

V. PATENTS

With but few exceptions, the patents which have been issued during the past
year are notable for absence of novelty. For the greater part, these patents
are concerned with improvements or modifications of patents which have been
discussed in earlier reviews in this series.

Liquid ammonia has been used as a solvent in a process for the separation of
butadiene (8) from hydrocarbon mixtures resulting from cracking operations.
A method for the production of crystalline reaction products of liquid ammonia
and aldose sugars containing at least five carbon atoms has been described by
Lorand (58). The reactions were effected under pressure at temperatures of
50° to 90°C. Aliphatic amines have been formed by the catalytic hydrogenation
of nitriles in liquid ammonia solution (9). Additional patents relating to the
production of melamine from dicyanodiamide (51, 79) and from guanidine or
biguanidine (78) have been issued. Hill and Kropa (43) have described a
process for the production of ketoximes by the interaction of ketones and
hydroxylamine (or its salts) in liquid ammonia.

A process for the etherification of methylated sorbitol syrup has been described
by Soltzberg (74). The material to be etherified is dissolved in liquid ammonia,
treated with an alkali metal to form metal salts, followed by removal of the
ammonia and addition of alkyl or aralkyl halides or alkyl sulfates in the presence
of an inert hydrocarbon diluent. Similar procedures have been employed in
the etherification of cellulose by reactions between alkali cellulosates and benzyl
chloride (63) or allyl halides (64).

Treatment of dispersions of cyanamide or of dicyanamide in liquid ammonia
with, for example, ammonium acetate (45) or ammonium nitrate (46) has been
used in the preparation of guanidine salts. Liquid ammonia has also been used

as a solvent in an extraction process (42) for the separation of salts such as guanidine nitrate from ammonia-insoluble salts of polybasic inorganic acids. Ammonium dithiocarbamate (44) has been produced by the interaction of carbon disulfide and liquid ammonia, and ammonium sulfamate (48) has been formed by the ammonolysis of alkali chlorosulfonates. Liquid ammonia solutions of the trihydrate of calcium nitrate have been employed in the pretreatment of gaseous ammonia used in the nitridation of steel (95). Ammonia has also been used as a solvent for ammonium nitrate in a process concerned with the incorporation of suitable sensitizers into ammonium nitrate for use as an explosive (10). Ammonium nitrite may be stored or transported with safety following treatment with liquid or gaseous ammonia at or below 0°C. under conditions such that the resulting solution has an ammonia content of approximately 30 per cent (96).

VI. GENERAL

Certain precautions to be observed in the handling of anhydrous liquid ammonia, together with information concerning suitable containers, have been discussed (65). It is of interest to note that a review of American literature relating to "the chemistry of solutions in liquid ammonia" has been published in the Russian language by Shatenshteĭn (71).

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SOME LESS FAMILIAR ASPECTS OF CARBOHYDRATE CHEMISTRY[1]

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The chemistry of the group of compounds familiarly known as the carbohydrates constitutes one of the most important chapters in the science of organic chemistry. That this is true follows from the fact that a number of the compounds belonging to this family are among the most essential substances that contribute to human existence. To appreciate the truth of this statement, one need only recall the place occupied in our dietary by glucose, cane sugar, and sugar of milk. The late Phoebus A. Levene (39) once remarked that "glucose is one of the most important substances in the economy of the world." When commenting in a similar vein with reference to the great importance of the carbohydrates, Emil Fischer (16) stated that "next to proteins no group of compounds is so important for the study of chemical processes in plant and animal life as the carbohydrates, and as foodstuffs they occupy first place without any question."

Not only do the carbohydrates command our attention on biological grounds, but as a group of chemical compounds they have made important contributions to organic chemical theory. An illustrious example of this is found in the two classical papers of Emil Fischer (16) entitled, "The Configuration of Grape Sugar and its Isomers," published just fifty years ago, in which, by the use of the van't Hoff concept of the asymmetric carbon atom, he added one of the most brilliant chapters that we have in the field of stereochemistry. The Semi-centennial of this notable event was most fittingly commemorated by the Division of Sugar and Sugar Technology of the American Chemical Society, at its meeting in St. Louis last Spring.

In these very momentous days in the world's history, the organic chemist is being constantly importuned to search among the several hundred thousand compounds of carbon which are already at his disposal, as well as among those new ones which are being constantly fabricated in his laboratory, for substances that will contribute to the welfare of human kind. It may be safely asserted that there never has been a time in which chemistry has been so close to the needs of man as it is at the present moment. Besides these synthetics, the chemist has at his disposal many organic compounds, or their easily obtained derivatives, that are found in abundance in Nature. Among these the field of carbohydrates makes its contribution in the form of glucose, sucrose, sugar of milk, starches, and cellulose. We need only to be reminded that some of these well-known sub-

stances arc being utilized as the basic materials in many of our important chemical enterprises.

The scientific research that has been necessary to establish the molecular architecture of glucose, the central compound of this family, has covered a period of approximately sixty years. Concurrently with this structural development has come a proportional increase in our knowledge concerning the behavior of the carbohydrates towards chemical reagents. In support of this assertion, one need only make a passing reference to the chemical and biological importance of the fundamental phenomena involved in the oxidation of the carbohydrates,— by which we mean the chemical life history of the sugar molecule as it is gradually being converted to carbon dioxide and water.

As is well known, the chemical behavior of the more simple carbohydrates towards many complex reagents is very well understood. Furthermore, the behavior of some very complex carbohydrates, like the starches and cellulose, in the presence of some simple substances, such as hydrochloric and sulfuric acids, seems also to be well understood. Yet the behavior of reducing carbohydrates towards such simple substances as the soluble bases has not been studied as extensively as the character of the reaction might seem to warrant.

An examination of the research literature in this field of scientific inquiry brings forth the names of Peligot (46, 48, 49) in the 1870's; of Cuisinier (8), Kiliani, and Scheibler in the 1880's; of de Bruyn and van Ekenstein in the 1890's; and of John Ulric Nef in the first fifteen years of this century. The following is a brief outline of the major achievements of these well-known men of other days and of some of the more recent implications of their work.

To facilitate the treatment of this subject, it has been found best to classify the chemical behavior of the reducing carbohydrates in alkaline solutions in the following manner:

The chemical behavior of the reducing sugars in alkaline solution

I. Polymerization of carbohydrates in alkaline solution to yield other carbohydrates
   A. Polymerization of glycolaldehyde to yield a tetrose: erythrose
   B. Polymerization of glyceraldehyde to yield ketohexoses: DL-fructose and DL-sorbose
   C. Polymerization of glyceraldehyde or its condensation with dihydroxyacetone to yield ketohexoses: D-fructose and D-sorbose
II. Rearrangement of carbohydrates in alkaline solution
   A. Rearrangements to form saccharinic acids and saccharins
      (1) Saccharinic acids and saccharins
      (2) Isosaccharinic acids and isosaccharins
      (3) Metasaccharin
      (4) Parasaccharin and parasaccharinic acid
   B. Rearrangement to form other carbohydrates: the de Bruyn and van Ekenstein transformation
   C. Rearrangements to form hypothetical sugar enediols

III. Degradation of carbohydrates in alkaline solution
  A. Fragmentation of the carbon chain
  B. Rearrangement of the fragments to other carbohydrates, saccharinic
    acids, and saccharins

I. POLYMERIZATION OF CARBOHYDRATES IN ALKALINE SOLUTION TO YIELD OTHER CARBOHYDRATES

A. Polymerization of glycolaldehyde to yield a tetrose: erythrose

The polymerization of carbohydrates by alkalies with the resulting formation of other carbohydrates has been accomplished in at least three notable cases. In 1892, Fischer and Landsteiner (18) treated an aqueous solution of glycolaldehyde cooled to 0°C. with sufficient sodium hydroxide to have the system finally contain 1 per cent of the base, and then allowed the reaction mixture to remain at 0°C. for 15 hr., when the glycolaldehyde disappeared. At the end of this time, the solution either did not react with Fehling's solution or, if at all, reacted only very slightly.

When the reaction mixture was acidified with acetic acid and then treated with phenylhydrazine, an osazone was obtained which was exceptionally similar to phenylerythrosazone. The analytical data were in harmony with theoretical demands.

The change in glycolaldehyde (55a) may be represented as follows:

$$2CH_2OHCHO \rightarrow CH_2OHCHOHCHOHCHO$$

B. Polymerization of glyceraldehyde to yield ketohexoses: DL-fructose and DL-sorbose

Ernst Schmitz (19, 20, 54) reported the formation of acrose through the action of 0.1 per cent of barium hydroxide upon DL-glyceraldehyde for 24 hr. As a result of this experiment, Schmitz obtained crystalline DL-fructose (α-acrose), and crystalline DL-sorbose (β-acrose). The DL-sorbose was easily soluble in methyl alcohol and was obtained crystalline for the first time.

C. Polymerization of glyceraldehyde or its condensation with dihydroxyacetone to yield ketohexoses: D-fructose and D-sorbose

H. O. L. Fischer and Erich Baer (20) reported a synthesis of D-fructose and D-sorbose from D-glyceraldehyde alone, or from D-glyceraldehyde and dihydroxyacetone. A solution of 6.16 g. of glyceraldehyde in 100 cc. of water, made alkaline with barium hydroxide to the extent of being 0.01 molar and containing 1 cc. of 0.1 N iodine solution per 13.75 cc., was allowed to stand at room temperature for 2 hr. The reaction was followed polarimetrically. At the end of this time, the barium ion was removed with sulfuric acid. The D-fructose was precipitated as calcium fructosate, from which compound the free sugar was liberated with carbon dioxide. After the filtrate was fermented to remove the last trace of D-fructose, D-sorbose was crystallized therefrom and identified by

means of its osazone. The total yield of the two ketohexoses was 90 to 95 per cent, and the ratio of the D-fructose to the D-sorbose was 1:1.

Fischer and Baer (*cf.* 51) were of the opinion that before the actual condensation could take place there must be a conversion in part of the D-glyceraldehyde into dihydroxyacetone. In fact, when a mixture of D-glyceraldehyde and dihydroxyacetone in the ratio of 1:1 was used, the reaction time was shortened from about 2 hr. to 40 min. That D-glyceraldehyde may be converted to dihydroxyacetone to the extent of 49 per cent in hot pyridine is an experimental fact.

The reactions may be expressed as follows:

$$
\begin{array}{ccc}
\begin{array}{c}
CH_2OH \\
| \\
CO \\
| \\
HOCH \\
| \\
H \\
\text{Dihydroxyacetone} \\
\\
H-C=O \\
| \\
HCOH \\
| \\
CH_2OH \\
\text{D-Glyceraldehyde}
\end{array}
&
\xrightarrow{OH^-}
&
\begin{array}{c}
CH_2OH \\
| \\
C=O \\
| \\
HOCH \\
| \\
HCOH \\
| \\
HCOH \\
| \\
CH_2OH \\
\text{D-Fructose}
\end{array}
\qquad
\begin{array}{c}
CH_2OH \\
| \\
C=O \\
| \\
HCOH \\
| \\
HOCH \\
| \\
HCOH \\
| \\
CH_2OH \\
\text{D-Sorbose}
\end{array}
\end{array}
$$

$$
\left[
\begin{array}{c}
CH_2OH \\
| \\
C=O \\
| \\
HCOH \\
| \\
HCOH \\
| \\
HCOH \\
| \\
CH_2OH \\
\text{D-Psicose}^2
\end{array}
\qquad
\begin{array}{c}
CH_2OH \\
| \\
C=O \\
| \\
HOCH \\
| \\
HOCH \\
| \\
HCOH \\
| \\
CH_2OH \\
\text{D-Tagatose}
\end{array}
\right]
$$
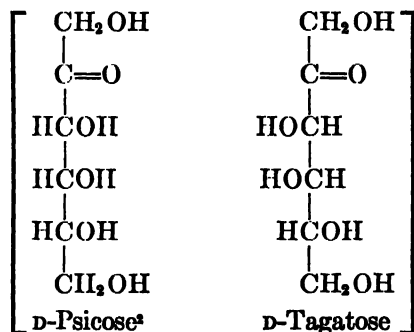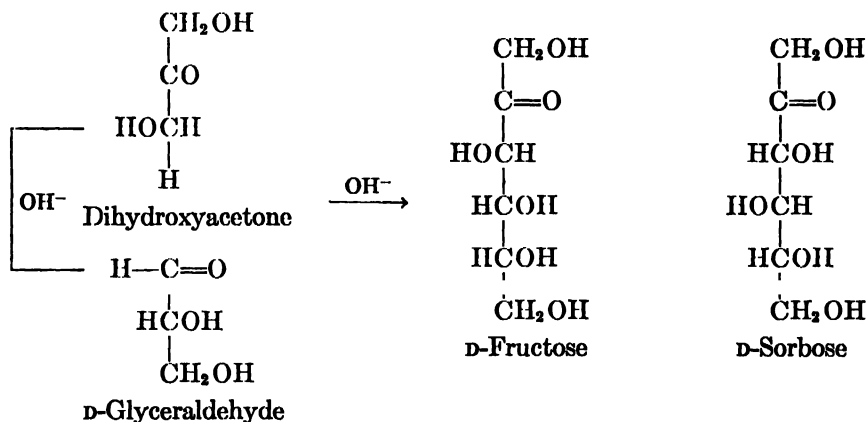
The ketoses formed from this aldol condensation are those that have the hydroxyl groups on carbon atoms 3 and 4 in the *trans* position to each other. D-Psicose[2] and D-tagatose were not formed.

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[2] Since the 2-D-ketohexose which is common to D-allose and D-altrose has been designated in the past either as D-pseudo-fructose or as D-psicose, the author proposes D-allulose as a more suitable name, in view of that the fact that the ending "ulose" is now used (40) to designate the 2-keto sugars except in those cases, such as D-fructose, D-tagatose, and D-sorbose, in which long-continued use has given these names priority. Even in these cases the names D-mannulose (or D-gluculose), D-talulose (or D-galactulose), and D-idulose (or D-gululose) would be easily understood. See reference 61.

II. REARRANGEMENT OF CARBOHYDRATES IN ALKALINE SOLUTION

A. Rearrangements to form saccharinic acids and saccharins

(1) *Saccharinic acids and saccharins:* The chemical reactions of the reducing sugars in alkaline solution which were carried out over a period of years when even the molecular structure of the simple sugars was not yet thoroughly understood are of much interest. The rearrangements of the hexoses to acids was the outstanding contribution in the period from 1879 to 1890.

One of the less familiar reactions of reducing sugars in alkaline solution is that group of rearrangements which yield the so-called saccharins and saccharinic acids. The term "saccharinic acids" was applied to those acids obtained through the rearrangement of either an aldose or a ketose when these latter compounds were subjected to alkaline conditions,—a chemical change which always yielded a desoxy acid, thus showing that an internal oxidation–reduction had taken place. The lactones of these desoxy acids were named saccharins.

In 1839 Peligot (47) reported the isolation, from a reaction mixture of lime and glucose, of a substance for which Dumas (5) proposed the name "glucic acid." However, it was not until 1879 that Cuisinier (8) announced the discovery of a non-fermentable, crystalline substance of bitter taste among the reaction products obtained by boiling an aqueous solution of glucose containing lime. He assigned the formula $C_{12}H_{22}O_{11}$ to it, but later Scheibler assigned the formula $C_6H_{12}O_6$, i.e., he designated the substance as an isomer of glucose.

Scheibler (52), in 1880, and Kiliani (25, 26, 29), in 1882, showed that fructose, invert sugar, and lactose could be used as well as glucose in the preparation of this new acid and its lactone. As a result of the efforts of these two workers these two compounds may be formulated as follows:

Saccharinic acid   Saccharin
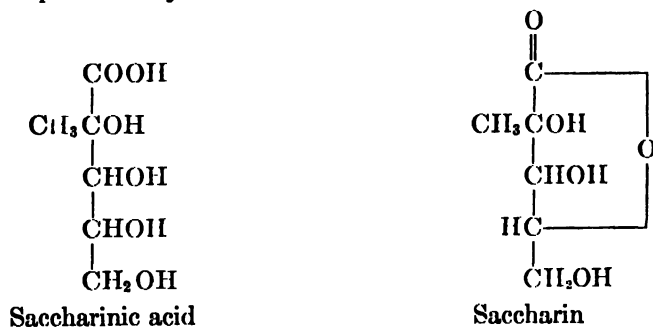
According to some of the theories (10, 29, 41, 45, 54) concerning the formation of the saccharinic acids, it is assumed that the configuration about the α-carbon atom of this acid arises from a benzilic acid rearrangement. Hence the saccharinic acid and its γ-lactone should exist in two forms,—namely, epimers,— formerly designated as α and β according as the hydroxyl group is on the right or left side, respectively, of the carbon atom to which they are bound.

(2) *Isosaccharinic acids and isosaccharins:* In 1882, Cuisinier (8) discovered a highly insoluble calcium salt of an acid, $C_6H_{12}O_6$, among the reaction products obtained by the action of lime on an aqueous solution of maltose; to this acid was given the name "maltic acid." Furthermore, he found that maltic acid lost

one molecule of water, thus giving rise to a lactone, $C_6H_{10}O_5$, which appeared to be analogous to the "saccharin" of Peligot; hence he called it isosaccharin, and the corresponding acid isosaccharinic acid. Cuisinier also prepared "isosaccharin" from lactose, and Kiliani (28) prepared it from galactose.

Gakhokidze (21), a Russian chemist, has just announced the synthesis of "saccharin" by the use of α-ketoarabonic acid and the appropriate Grignard technique.

We are indebted to Kiliani (30, 31) for our knowledge of the structure of these compounds. An interesting relationship is shown between the "isosaccharinic acids" and "isosaccharins" of D-glucose and D-galactose in the following diagram. Obviously these are the only ones theoretically possible in the D-hexose series of sugars.

Rearrangement of the hexoses to saccharinic acids

CHO	COOH	COOH	CHO
HCOH	HOH₂CCOH	HOCCH₂OH	HCOH
HOCO	CH₂	CH₂	HOCH
HCOH	HCOH	HCOH	HOCH
HCOH	CH₂OH	CH₂OH	HCOH
CH₂OH			CH₂OH
D-Aldehydo-glucose	α-Isosaccharinic acid	β-Isosaccharinic acid	D-Aldehydo-galactose
	or	or	
	D-α-hydroxy-methyl-3-desoxy-ribonic acid	D-β-hydroxy-methyl-3-desoxy-arabonic acid	

α-Isosaccharin
or
D-α-hydroxymethyl-3-desoxy-
ribonic-γ-lactone

β-Isosaccharin
or
D-β-hydroxymethyl-3-desoxy-
arabonic-γ-lactone

(*3*) *Metasaccharin:* In 1883, Kiliani (27, 28, 33, 35, 36) also discovered a new saccharinic acid, $C_6H_{12}O_6$, from a reaction mixture consisting of lactose (1 kg.), water (9 kg.), and calcium hydroxide (450 g.) from which he hoped to obtain enough "isosaccharinic acid" for studies of molecular structure. The new calcium salt was found in the filtrate from the highly insoluble calcium isosaccharinate. The analysis of this new calcium salt, $Ca(C_6H_{11}O_6)_2 \cdot 2H_2O$, as well as the analytical data of the anhydrous compound, were in highly satisfactory agreement with the demands of the empirical formula. When the crystals of the new acid were isolated, they were found to have a bitter taste and a composition corresponding to the lactone, $C_6H_{10}O_5$. Since the properties of this new compound were quite different from those of Peligot's "saccharin" and Cuisinier's "isosaccharin," Kiliani named it "metasaccharin." The molecular structures of "metasaccharinic acid" and "metasaccharin" showed that each had a normal chain, and that carbon atom 3 was the desoxy one (34).

COOH
|
CHOH
|
CH₂
|
CHOH
|
CHOH
|
CH₂OH
Metasaccharinic acid
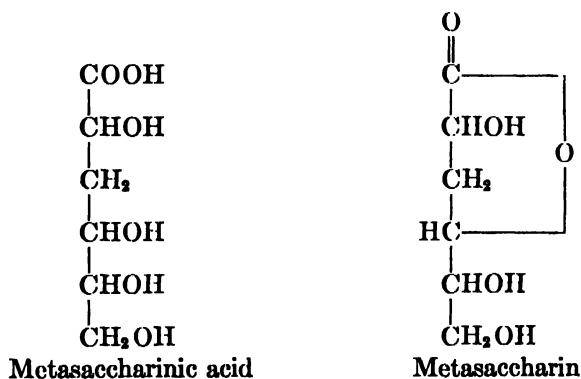
Metasaccharin

(*4*) *Parasaccharin and parasaccharinic acid:* Kiliani and Sanda (35) reported a fourth saccharinic acid in the mother liquor from the calcium metasaccharinate obtained from an aqueous solution of galactose and lime. After removing the excess calcium from the mother liquor and then extracting the lactic acid with ether, an attempt was made to form salts of organic bases with the remaining acid material. This technique was unsuccessful. A barium salt of doubtful purity was prepared, however. After a very laborious investigation of the character of the acidic material, Kiliani and Loeffler (32) assigned the following formula:

CH₂OH
|
CH₂
|
C—OH
| ＼COOH
CHOH
|
CH₂OH
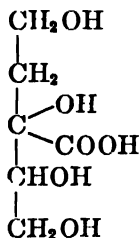
In 1910, Nef (42) took issue with the formula of Kiliani, and pointed out that Kiliani's "parasaccharinic acid" was α-D-galactometasaccharinic acid, the epimer of β-D-galactometasaccharinic acid, previously described. Later Kiliani withdrew his views concerning parasaccharinic acid. More extended reference will be made to these compounds later in our discussion.

B. Rearrangement to form other carbohydrates: the de Bruyn and van Ekenstein transformation

One of the most important rearrangements which reducing monosaccharides undergo in alkaline solutions is that described by Lobry de Bruyn and Alberda van Ekenstein (7) in a series of papers published in the 1890's. These were occasioned by an observation of de Bruyn (6), who had noted that the optical rotatory power of dilute solutions of glucose containing small concentrations of potassium hydroxide diminished in value over a period of time and finally tended toward 0°. The velocity of this transformation was accompanied by a change in the concentration of the alkali as well as by changes in temperature.

de Bruyn and van Ekenstein demonstrated experimentally that the almost inactive sirup which they had obtained by the action of either potassium, sodium, or ammonium hydroxide on glucose was formed equally well by the use of lime, magnesia, sodium carbonate, or potassium carbonate. Hence, they concluded that it was a matter of the hydroxyl ion and not the nature of the special alkaline material used that yielded the common product. In commenting upon the probable cause of the change taking place in the optical character of mildly alkaline solutions of glucose, de Bruyn suggested that it might be due to a "change in the sign of the CHOH group adjacent to the aldehyde group", in quite the same way as the change observed in many sugar acids when solutions of them in either quinoline or pyridine are heated or—in present-day parlance—when a sugar is epimerized. de Bruyn and van Ekenstein not only confirmed this conjecture of de Bruyn,—namely, that in mildly alkaline solutions glucose was converted into mannose,—but furthermore showed that the ketohexose, fructose, corresponding to these two aldohexoses was also formed at the same time. They were able to show experimentally that these three sugars, glucose, mannose, and fructose, were reciprocally interconvertible in mildly alkaline solutions.

When these investigators treated solutions of glucose with lead hydroxide, they obtained mannose only. They furthermore discovered that fructose in the presence of lead hydroxide was not converted into either of its corresponding aldo sugars, glucose and mannose. If mannose is formed, it is present in exceedingly small quantities. In seeking the cause for this difference in the behavior of these three well-known sugars in the presence of lead hydroxide, a guarded suggestion was made concerning the possible formation of another ketohexose. It will be shown below that Kuzin's structure for the enemonol obtained from glucose and lime could form mannose but no fructose if the ring of the enol remains stable, while, on the other hand, it is easily conceivable that mannose and fructose could be formed from the glucose 1,2-enediol which is produced in solutions of sodium hydroxide.

Later, de Bruyn and van Ekenstein made an examination of the products ob-

tained by heating a solution of galactose with potassium hydroxide. They believed that the reaction mixture contained galactose, talose, tagatose, D-sorbose, and galtose. In a similar experiment with glucose, they reported the following reaction products: glucose, mannose, fructose, allulose[3], and glutose. They were unable to crystallize glutose after many attempts with different solvents. Owing to the difficulty in establishing that glutose and galtose were definite compounds, de Bruyn and van Ekenstein stated that "... it is not improbable that the glutoses and galtoses might be mixtures."

Spoehr and Strain (55) reported that "in an extensive series of experiments on the formation of glutose from hexoses and invert sugar with Pb(OH)₂, and also with phosphates, involving many kilos of glucose, no strictly uniform products were obtained." These well-known investigators found "... great variations in the yields of non-fermentable residues, in the reducing power of these, and in their aldose content...." The glutose osazone was shown to be a *mixture* of phenylhydrazine derivatives.

Zerban and Sattler (51, 60, 61), of the New York Sugar Trade Laboratory and Brooklyn College, when studying the composition of a sample of distillery residue, succeeded in isolating an osazone fraction the data for melting point, molecular weight, specific rotation, and mutarotation of which positively identify it with the osazone of allulose (psicose), previously described by Steiger and Reichstein. Other sugars appear to be present in the distillery residue.

More recently, Wolfrom and Lewis (59) established experimental conditions for the conversion of D-glucose in lime water at 35°C. into a mixture of D-glucose, D-mannose, and D-fructose with a negligible amount of formation of a possible saccharinic acid. A molar solution of D-glucose under such conditions attained polarimetric equilibrium on standing for 10 days at room temperature. The pH of the lime water dropped from 12.6 to 10.6 on the addition of the glucose. The solution stood for a year without developing any free acidity. The composition of the reaction product was as follows:

	per cent
D-Glucose	63.4
D-Fructose	30.9
D-Mannose	2.4
Non-sugar substances, probably saccharinic acids	3.3
	100.0

In 1930, Montgomery and Hudson (40), after making certain improvements in this transformation, succeeded in showing that a solution of lactose when kept at a temperature of 35°C. for 36 hr. had undergone a change in the specific rotation from 52.5° to 31.6°, at which value it was constant. After the reaction mixture had been worked up a final product was obtained which was crystalline and exhibited mutarotation in changing from $[\alpha]_D = -23.8°$ to $-51.5°$ (constant in 2 min.). The new substance proved to be the keto sugar of lactose and was named β-D-lactulose.

In 1930, Austin (1) succeeded in obtaining D-glucoheptulose by the reaction of D-glucoheptose, a seven-carbon-atom monosaccharide, in lime water.

[3] See footnote 2, page 540.

C. *Rearrangements to form hypothetical sugar enediols*

It has been asserted that ninety-three different kinds of reaction products are theoretically possible when D-glucose is acted upon by a strong base. In spite of the exceedingly complex character of the systems that form under these conditions, it has been found possible to coördinate their chemical behavior by postulating the rearrangement of the cyclic sugars into acyclic ones, which under the alkaline conditions give rise to enediolic structures of the reducing sugar itself. In the following sections of this review an attempt has been made to present a more unified picture of the chemical systems under discussion when they are considered from this theoretical point of view.

The enediolic concept of molecular structure in reducing sugars is not a new one. As long ago as 1870, Hlasiwetz and Habermann (24), in accounting for the formation of glucose tetraacetate through the interaction of glucose and acetic anhydride, assigned an enediolic structure to the glucose molecule which they represented as a 3,4-enediol, $CH_2OHCHOHC(OH)\!\!=\!\!C(OH)CHOH\text{-}CH_2OH$. Again, in 1895 Emil Fischer (17) expressed the opinion that the glucose molecule underwent enolization in a sodium hydroxide solution. The soluble reaction product was thought to be sodium glucosate, to which Fischer gave the formula $CH_2OHCHOHCHOHCHOHC(OH)\!\!=\!\!CHONa$. When this solution was acidulated with acetic acid and treated with phenylhydrazine, glucosazone was easily obtained.

In 1900, Wohl and Neuberg (58) postulated the existence of a commonly formed intermediate in order to account for the conversion of glyceraldehyde, $CH_2OHCHOHCHO$, and dihydroxyacetone, $CH_2OHCOCH_2OH$, in alkaline solution to lactic acid, $CH_3CHOHCOOH$. They assumed the intermediate to be a triose enediol, as indicated below:

$$
\begin{array}{ccccc}
\text{CHO} & & \text{CHOH} & & \text{CH}_2\text{OH} \\
| & & \parallel & & | \\
\text{CHOH} & \longrightarrow & \text{COH} & \longleftarrow & \text{CO} \\
| & & | & & | \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
\text{Glyceraldehyde} & & \text{Triose enediol} & & \text{Dihydroxyacetone}
\end{array}
$$

$$\downarrow$$

$$CH_3CHOHCOOH$$
$$\text{Lactic acid}$$
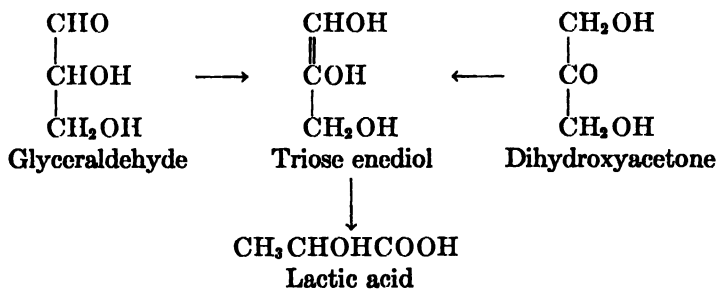
These authors indicated that a similar relationship should hold for glucose, mannose, and fructose.

In his exhaustive experimental studies on the behavior of certain reducing sugars towards strong bases, Nef (41) in 1910 extended the enediolic concept of the formula for the reducing sugars. The elaboration of this principle afforded Nef an opportunity to elucidate and coördinate the mechanism of the many reactions taking place under such conditions. In the case of glucose, he postulated the existence not only of the 1,2-enediol of that hexose, but also of the 2,3- and 3,4-enediols. More extended reference will be made to these compounds below.

In an experimental study of the catalytic influence which the monosaccharides exert on the condensation of formaldehyde, Kuzin assumed that the enolic form of the sugar which is produced under these conditions is the catalytically active form. Earlier workers had concluded that the common hydroxyl ion in these solutions was the enolizing agent, regardless of the character of the cations. Kuzin (37, 38) found no difference at 60°C. between the effect produced by either calcium hydroxide or sodium hydroxide, but at 35–37°C. the condensation had hardly set in by the use of sodium hydroxide before it had been brought to completion by the use of calcium hydroxide. That the reaction of glucose in the presence of each of these common bases follows two different courses is shown by the fact that under the same experimental conditions with calcium hydroxide on the one hand, and a mixture of sodium hydroxide and disodium hydrogen phosphate with a pH corresponding to that of calcium hydroxide (i.e., 12) on the other, no substance showing reducing power in the acidulated solution could be detected.

In view of these facts concerning the influence of the nature of the cations in glucose solutions, Kuzin postulated that the differences were due to the presence of two different enolic compounds. In those cases where calcium hydroxide is used, the reaction results in the formation of a cyclic enemonol, and where sodium hydroxide is used, an acyclic enediol is formed with a negatively charged ion. Kuzin gives the following reactions for their formation:

D-Glucose   Calcium D-glucosate

2-Hydroxy-1,2-glucoseen
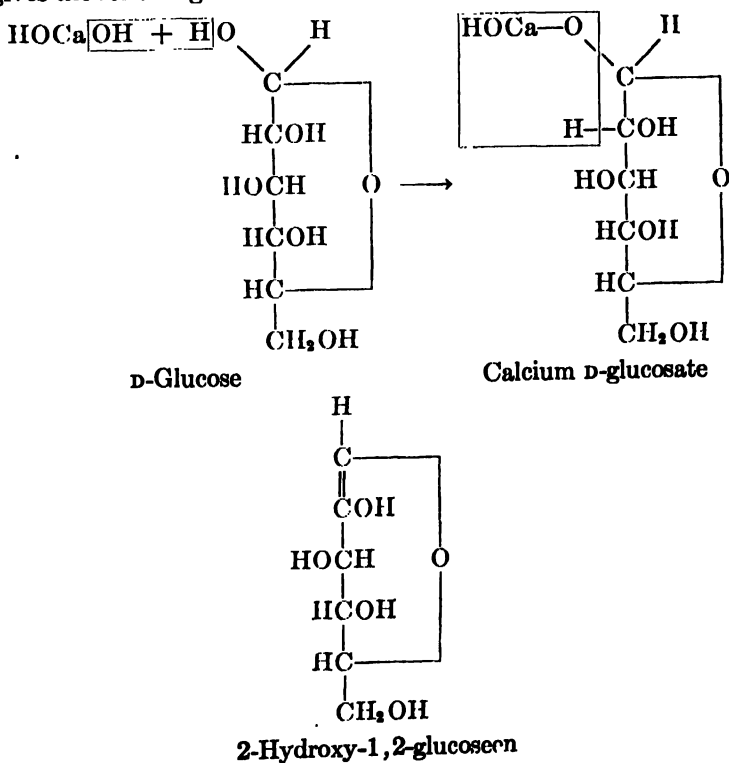
It is obvious that 2-hydroxy-1,2,-glucoseen could form mannose by the addition of water, but it could not form fructose without a rupture of the ring. In the following equation, it is clear that either mannose or fructose could be so formed.

$$
\begin{array}{ccc}
& H & H & H \\
& | & | & | \\
Na^+ + \boxed{-OH\ H}OC- & Na^+ + -O-C-O^- & C--O^- + Na^+ \\
& | & || \\
HCOH & H-COH & COH \\
| & | & | \\
HOCH\ \ O \longrightarrow & HOCH \longrightarrow HOCH \\
| & | & | \\
HCOH & HCOH & HCOH \\
| & | & | \\
HC- & HCOH & HCOH \\
| & | & | \\
CH_2OH & CH_2OH & CH_2OH \\
\text{D-Glucose} & & \text{Sodium 1,2-enediol-} \\
& & \text{glucosate}
\end{array}
$$
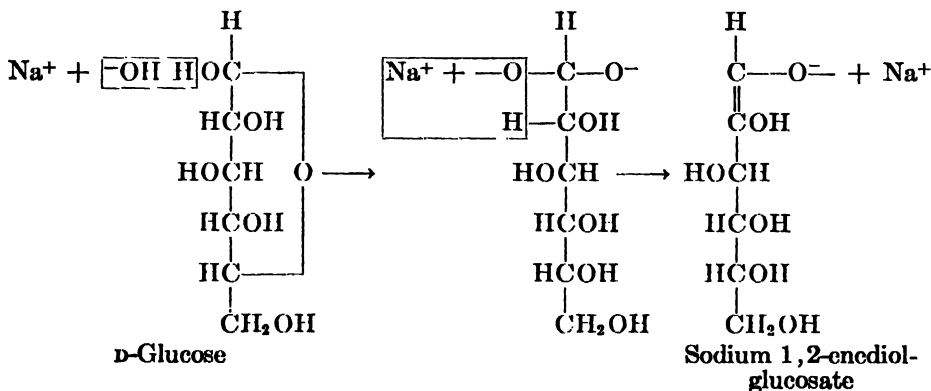
These proposals of Kuzin would harmonize with the experimental data of de Bruyn and van Ekenstein with reference to the action of lead hydroxide on D-glucose.

An enediolic form of the common non-aromatic reducing sugars has as yet never been isolated and characterized. Euler and Martius, by heating a strongly alkaline solution of glucose to 90°C. under a stream of nitrogen, obtained a crystalline reaction product to which they assigned the enediolic formula of tartronic aldehyde, $CHOH=C(OH)CHO$, and which they named "reductone". The chief interest in this compound arises from the fact that it is either a possible decomposition product of glucose 1,2-enediol, or it might be considered a fragmentation product of the glucose molecule which had subsequently been enolized. The former possibility is very highly probable, for reasons given below.

In the aromatic series, the diacetate of the common enediol of mandelic aldehyde, $C_6H_5CHOHCHO$, and of benzoylcarbinol, $C_6H_5COCH_2OH$, which, after the manner of the nomenclature adopted by Votoček for the methyloses, may be designated as aldoglycerophenylose and ketoglycerophenylose, respectively, has recently been prepared as the diacetate by Dauben, Evans, and Meltzer (9), i.e., glycerophenylose enediol diacetate.

$$
\begin{array}{c}
CHOCOCH_3 \\
|| \\
COCOCH_3 \\
| \\
C_6H_5
\end{array}
$$
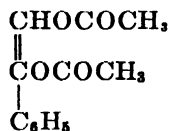
Further reference will be made below to the hexose enediols.

III. DEGRADATION OF CARBOHYDRATES IN ALKALINE SOLUTION

A. Fragmentation of the carbon chain

It has long been a matter of common knowledge that the carbon chain in the glucose molecule will undergo fragmentation (3,42) into compounds containing a smaller number of carbon atoms than the sugar itself when the latter is allowed to react with solutions of alkaline substances. In fact, the change may be a very drastic one, as was so well shown by Benedict (2) when he heated a 1 per cent

solution of glucose for 1 min. with one-half its volume of a 10 per cent solution of potassium hydroxide and obtained a reaction, or a series of reactions, which caused the glucose solution to lose its reducing power towards Fehling's solution. It was this latter observation which prompted Benedict to formulate the well-known more sensitive alkaline copper solution which now bears his name.

When glucose solutions contain appropriate concentrations of some strong base, such as potassium hydroxide, sodium hydroxide, tetramethylammonium hydroxide, or benzyltrimethylammonium hydroxide, and also when such reaction mixtures are maintained at appropriate temperatures, a fragmentation of the carbon chain of the glucose takes place, –a chemical change that produces compounds which undergo reactions of their own with the alkali present to give lactic acid as one of the final reaction products.

The most thorough investigation of the character of the reaction products formed in this type of chemical inquiry was that of John Ulric Nef (42). These researches of Professor Nef were a fitting finale to a brilliant career as an experimentalist and theorist. In the earlier period of his academic work he carried on a series of experiments on the reactions of the cyanides and the isocyanides. During this period he established the now well-known structural formula for fulminic acid, namely, HONC. As a general deduction of his studies with the isocyanides and fulminic acid, however, he was convinced that in these compounds the carbon atom in the NC radical was bivalent and hence intensely reactive.

By reason of his views concerning the valence of carbon in certain compounds, Nef gradually evolved a generalized theory of organic chemical behavior, the central theme of which postulated that an intermediate compound of fugitive existence was always formed in organic chemical reactions and that this intermediate compound contained the highly reactive bivalent carbon. This highly reactive intermediate could undergo a number of reactions, such as a rearrangement to a more stable form, polymerization to an unsaturated compound, or addition of reagents.

Hence, it is not strange that from these views Nef should have quickly perceived the significance of the enolic transformation of the reducing sugars in alkaline solutions. As stated above, he greatly extended the views of Hlasiwetz and Habermann, Emil Fischer, and Wohl and Neuberg, by postulating the existence of the following enediolic structures of D-glucose in alkaline solution:

CHO	CHOH	CH$_2$OH	CH$_2$OH
HCOH	COH	COH	HCOH
HOCH	HOCH	COH	COH
HCOH	HCOH	HCOH	COH
HCOH	HCOH	HCOH	HCOH
CH$_2$OH	CH$_2$OH	CH$_2$OH	CH$_2$OH
D-Glucose	D-Glucose 1,2-enediol	D-Glucose 2,3-enediol	D-Glucose 3,4-enediol
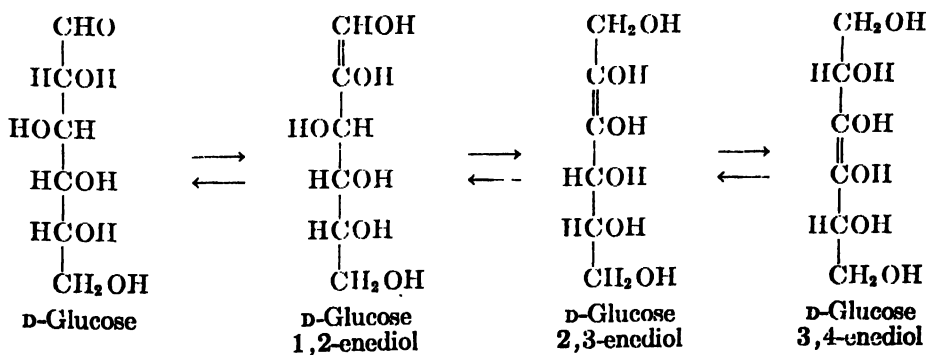
This investigator furthermore assumed that these enediolic structures under appropriate conditions of alkalinity and temperature would undergo fragmentation at the double bond, a reaction which would give the postulated fugitive intermediate containing the highly reactive bivalent carbon atom. These supposed changes are indicated in the following equations:

$$
\begin{array}{c}
\text{CHOH} \\
\parallel \\
\text{COH} \\
\mid \\
\text{HOCH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{CH}_2\text{OH}
\end{array}
\quad\longrightarrow\quad
\begin{array}{c}
-\text{COH} \\
\mid \\
\text{HOCH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{CH}_2\text{OH}
\end{array}
\quad + \quad
\begin{array}{c}
\text{H} \\
\diagdown \diagup \\
\text{C} \\
\diagup \diagdown \\
\text{OH}
\end{array}
\qquad (1)
$$

D-Glucose 1,2-enediol   D-Arabinose (active form)   Formaldehyde (active form)

$$
\begin{array}{c}
\text{CH}_2\text{OH} \\
\mid \\
\text{COH} \\
\parallel \\
\text{COH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{CH}_2\text{OH}
\end{array}
\quad\longrightarrow\quad
\begin{array}{c}
-\text{C}-\text{OH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{CH}_2\text{OH}
\end{array}
\qquad
\begin{array}{c}
-\text{C}-\text{OH} \\
\mid \\
\text{CH}_2\text{OH}
\end{array}
\qquad (2)
$$

D-Glucose 2,3-enediol   D-Erythrose (active form)   Glycolaldehyde (active form)

$$
\begin{array}{c}
\text{CH}_2\text{OH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{COH} \\
\parallel \\
\text{COH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{CH}_2\text{OH}
\end{array}
\quad\longrightarrow\quad
2\,
\begin{array}{c}
-\text{C}-\text{OH} \\
\mid \\
\text{HCOH} \\
\mid \\
\text{CH}_2\text{OH}
\end{array}
\qquad (3)
$$

D-Glucose 3,4-enediol   Glyceraldehyde (active form)

In recent times, however, we are confronted with the now-known bond energy involved in a double bond of carbon to carbon as compared to that of the single bond of carbon to carbon, i.e., the doubly bound carbon atoms are more strongly linked than the singly bound. Hence, the fragmentation cannot take place as indicated. Furthermore, the work of Schmidt (43, 53) and others clearly shows that the formation of the double bond in a compound weakens the single bond of

carbon to carbon in the α, β-position to the double bond, and hence it is at that point that such compounds undergo fragmentation. In harmony with these points of view, the fragmentation of the enediolic forms of D-glucose should occur as follows:

$$
\begin{array}{l}
\text{CHOH} \\
\parallel \\
\text{COH} \\
| \\
\text{HOCH} \\
| \\
\text{HCOH} \\
| \\
\text{HCOH} \\
| \\
\text{CH}_2\text{OH}
\end{array}
\longrightarrow
\begin{array}{l}
\text{CHO} \\
| \\
\text{HCOH} \\
| \\
\text{CH}_2\text{OH} \\
\text{Glyceraldehyde}
\end{array}
+
\begin{array}{l}
\text{CHOH} \\
\parallel \\
\text{COH} \\
| \\
\text{CH}_2\text{OH} \\
\text{Triose} \\
\text{enediol}
\end{array}
\qquad (1')
$$

D-Glucose
1,2-enediol

$$
\begin{array}{l}
\text{CH}_2\text{OH} \\
| \\
\text{COH} \\
\parallel \\
\text{COH} \\
| \\
\text{HCOH} \\
| \\
\text{HCOH} \\
| \\
\text{CH}_2\text{OH}
\end{array}
\longrightarrow
\begin{array}{l}
\text{CH}_2\text{OH} \\
| \\
\text{COH} \\
\parallel \\
\text{COH} \\
| \\
\text{CH}_2\text{OH}
\end{array}
+
\begin{array}{l}
\text{CHO} \\
| \\
\text{CH}_2\text{OH}
\end{array}
\qquad (2')
$$

D-Glucose   Erythrose   Glycolaldehyde
2,3-enediol   2,3-enediol

$$
\begin{array}{l}
\text{CH}_2\text{OH} \\
| \\
\text{HCOH} \\
| \\
\text{COH} \\
\parallel \\
\text{COH} \\
| \\
\text{HCOH} \\
| \\
\text{CH}_2\text{OH}
\end{array}
\longrightarrow
\begin{array}{l}
\text{CH}_2\text{OH} \\
| \\
\text{COH} \\
\parallel \\
\text{COH} \\
| \\
\text{HCOH} \\
| \\
\text{CH}_2\text{OH}
\end{array}
+ \text{HCHO}
\qquad (3')
$$

D-Glucose   D-Arabinose   Formaldehyde
3,4-enediol   2,3-enediol

It is conceivable that the enediols of glyceraldehyde, erythrose, and arabinose may rearrange to the normal form and that in the cases of erythrose and arabinose these normal forms may undergo a different enolization and subsequent fragmentation. It is also clear that D-arabinose 2,3-enediol in equation 3' may undergo fragmentation into formaldehyde and erythrose 2,3-enediol before any rearrangement takes place to the normal form.

In one experiment Nef obtained from 100 g. of D-glucose in 8 N sodium

hydroxide, 40–45 g. of lactic acid, 15–10 g. of DL-α-hydroxybutyrolactone, 25 g. of other saccharins which consist chiefly of α- and β-D-dextrometasaccharins, about 2 g. of isosaccharin, and very little tar. He regularly obtained about 80 g. of non-volatile saccharins. The saccharins obtained are formulated in the following structures:

Products of rearrangement and fragmentation of D-glucose in alkaline solution

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{C} \\
| \\
\text{HCOH} \\
| \\
\text{HCH} \\
| \\
\text{HC} \\
| \\
\text{HCOH} \\
| \\
\text{CH}_2\text{OH}
\end{array}
$$
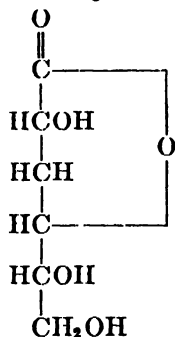
α-*d*-Dextrometasaccharin
or
D-3-desoxygluconic-γ-lactone

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{C} \\
| \\
\text{HOCH} \\
| \\
\text{HCH} \\
| \\
\text{HC} \\
| \\
\text{HCOH} \\
| \\
\text{CH}_2\text{OH}
\end{array}
$$
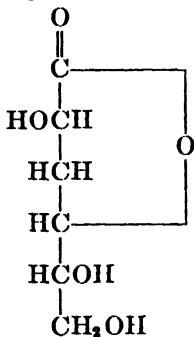
β-*d*-Dextrometasaccharin
or
D-3-desoxymannonic-γ-lactone
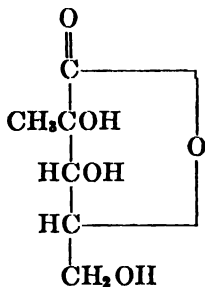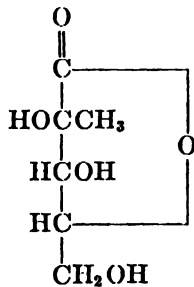
$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{C} \\
| \\
\text{CH}_3\text{COH} \\
| \\
\text{HCOH} \\
| \\
\text{HC} \\
| \\
\text{CH}_2\text{OH}
\end{array}
$$

α-*d*-Dextrosaccharin
or
D-β-methylribonic-γ-lactone

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{C} \\
| \\
\text{HOCCH}_3 \\
| \\
\text{HCOH} \\
| \\
\text{HC} \\
| \\
\text{CH}_2\text{OH}
\end{array}
$$

β-*d*-Dextrosaccharin
or
D-α-methylarabonic-γ-lactone

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{C} \\
| \\
\text{HOH}_2\text{CCOH} \\
| \\
\text{HCH} \\
| \\
\text{HC} \\
| \\
\text{CH}_2\text{OH}
\end{array}
$$

α-*d*-Isosaccharin
or
D-β-hydroxymethyl-3-desoxy-
ribonic-γ-lactone

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{C} \\
| \\
\text{HOCCH}_2\text{OH} \\
| \\
\text{HCH} \\
| \\
\text{HC} \\
| \\
\text{CH}_2\text{OH}
\end{array}
$$

β-*d*-Isosaccharin
or
D-α-hydroxymethyl-3-desoxy-
arabonic-γ-lactone

$$
\begin{array}{cc}
\text{COOH} & \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \\
\text{CHOH} & \text{CHOH} \\
\text{CH}_3 & \text{CH}_2 \\
 & \text{CH}_2
\end{array}
$$

<div align="center">

DL-Lactic acid   DL-α-hydroxybutyrolactone

or

DL-α-hydroxypropionic acid

</div>
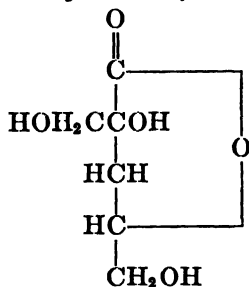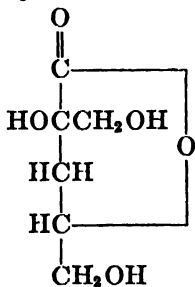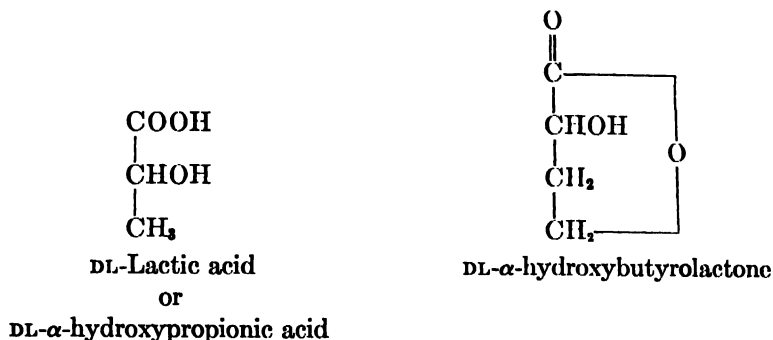
The chemical behavior of the reducing sugars in alkaline solutions, when examined from the standpoint of such experimental conditions as temperature, alkali normality, and the concentration of the carbohydrate used, has received only a limited amount of study. However, much can be learned with reference to the reactions of sugar molecules by reason of changes in these experimental conditions, because the amounts of the reaction products present which contain less than six carbon atoms shed much light on the course of the reaction. Furthermore, from the previous discussion concerning the nature of the saccharinic acids and the saccharins, it is clear that the total amount of these must be a measure of the extent to which the carbohydrate molecule has undergone rearrangement. Hoff (13) has shown experimentally that the amount of β-metagalactosaccharinic acid obtained from an alkaline solution of D-galactose is a function of the temperature and of the normality of the base.

Hence, we must conclude that there are two general directions in which a hexose molecule will react,—it may rearrange, or it may undergo fragmentation; i.e.,

<div align="center">

Rearrangement ← Molecule of reducing sugar → Fragmentation

</div>
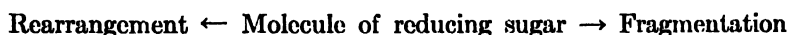
The formation of lactic acid under alkaline conditions has been experimentally studied by a number of investigators. The reactions (on page 554) leading to the formation of this acid from glucose, fructose, and mannose are those which have received general acceptance.

In these experiments, the lactic acid was extracted from the acidulated reaction mixture with ether and was then weighed as zinc lactate trihydrate, $Zn (C_3H_5O_3)_2 \cdot 3H_2O$. This salt was dehydrated and again weighed, and finally it was roasted to zinc oxide, and weighed for the third time. (a) Among the soluble bases used in this kind of work were potassium hydroxide, sodium hydroxide, tetraethylammonium hydroxide, benzyltrimethylammonium hydroxide, $(H_2N)_3COH$, and $(CH_3)_3SOH$, at temperatures of 25°, 50°, and 75°C. (b) The yields of lactic acid from D-glucose, D-mannose, and D-fructose in potassium hydroxide solutions at 50°C. rise sharply to approximately 3 N potassium hydroxide, after which they increase very slowly (13, 14, 14a). In the case of glucose the reaction produces 1 mole of lactic acid per mole of sugar used at 7 N (theory = 2 moles of lactic acid per mole of glucose used) and a temperature of 50°C. The highest yield of lactic

The conversion of D-gluco-, D-manno-, and D-fructo-pyranoses into DL-lactic acid

CHOH
HOCH
HOCH
HCOH
HC—O
CH₂OH
D-Mannopyranose

→

CHO
HOCH
HOCH
HCOH
HCOH
CH₂OH
D-Aldehydomannose

CHOH
HCOH
HOCH
HCOH
HC—O
CH₂OH
D-Glucopyranose

→

CHO
HCOH
HOCH
HCOH
HCOH
CH₂OH
D-Aldehydoglucose

HO—C—CH₂OH
HOCH
HCOH
HCOH
CH₃
D-Fructopyranose

→

CH₂OH
CO
HOCH
HCOH
HCOH
CH₂OH
D-Ketofructose

CHOH
COH
HOCH
HCOH
HCOH
CH₂OH
D-Glucose 1,2-enediol

→

CHO
CHOH
CH₂OH
Glyceraldehyde

+

CHOH
C—OH
CH₂OH
Triose enediol

→

$HC\!\!<^{OH}_{OH}$
CO
CH₃
Pyruvaldehyde hydrate

→

COOH
CHOH
CH₃
DL-Lactic acid

acid in these experiments was 1.2 moles (56) per mole of glucose at 25°C. when the base used was benzyltrimethylammonium hydroxide. (c) At 75°C., D-glu-cose, D-mannose, and D-fructose gave approximately the same amounts of lactic acid (14a), i.e., 0.7 mole per mole of sugar used,—a fact which would seem to in-dicate the same amount of a common precursor, namely, D-glucose 1,2 enediol. (d) The relative yields due to changes in temperature are given here in the order of their decreasing values, 37.5°C. > 50°C. > 62.5°C. > 25°C., over an alkaline range of approximately 0.5 N to 6.5 N.

As the experiment stands, these well-known hexoses yield lactic acid in the presence of soluble bases. In the above equations D-aldehydoglucose, D-glucose 1,2-enediol, glyceraldehyde, triose enediol, and pyruvaldehyde are assumed to be intermediate steps involved in the conversion of D-glucopyranose into lactic acid. The D-aldehydoglucose, glyceraldehyde, and pyruvaldehyde give *lactic acid* under the same experimental conditions, while D-glycopyranose (13, 14, 14a), aldehy-doglucose (50), glyceraldehyde (23), and its keto sugar, dihydroxyacetone (4, 12), yield pyruvaldehyde in the same way. Up to the present the hexonic enediols have not yet been isolated and characterized, but that they exist in such systems as these being studied has been pointed out above.

When a 0.25 M solution of maltose (11) is subjected to the same experimental conditions of temperature and alkali normality as an equivalent solution of glucose (i.e., 0.5 M), it has been found that the yields of lactic acid from maltose at 25° and 50°C. are approximately one-half of those obtained from glucose. By reason of the molar concentration chosen for both sugars, the amount of lactic acid formed in each case would be the same provided the disaccharide hydrolyzed

$$
\begin{array}{ll}
\begin{array}{l}
\text{CHOH} \\
| \\
\text{HCOH} \\
| \\
\text{HOCH} \quad \text{O} \\
| \\
\text{HCO}\!-\!\!-\!\!-\!\!\cdots\text{Gl} \\
| \\
\text{HC}\!-\!\!-\!\!-\!\!- \\
| \\
\text{CH}_2\text{OH} \\
\text{Maltose}
\end{array}
\longrightarrow
&
\begin{array}{l}
\text{CHO} \\
| \\
\text{HCOH} \\
| \\
\text{HOCH} \\
| \\
\text{HCO}\!-\!\text{Gl} \\
| \\
\text{HCOH} \\
| \\
\text{CH}_2\text{OH} \\
\text{Aldehydomaltose}
\end{array}
\longrightarrow
\end{array}
$$

$$
\begin{array}{l}
\text{CHO} \\
| \\
\text{HOCH} \\
| \\
\text{HCO}\!-\!\text{Gl} \; + \; \text{H}_2\text{CO} \\
| \\
\text{HCOH} \\
| \\
\text{CH}_2\text{OH} \\
\text{3-Glucosidoarabinose}
\end{array}
\longrightarrow
\begin{array}{l}
\text{CHO} \\
| \\
\text{HCO}\!-\!\text{Gl} \\
| \quad\quad\quad + \; \text{H}_2\text{CO} \\
\text{HCOH} \\
| \\
\text{CH}_2\text{OH} \\
\text{2-Glucosidoerythrose}
\end{array}
$$
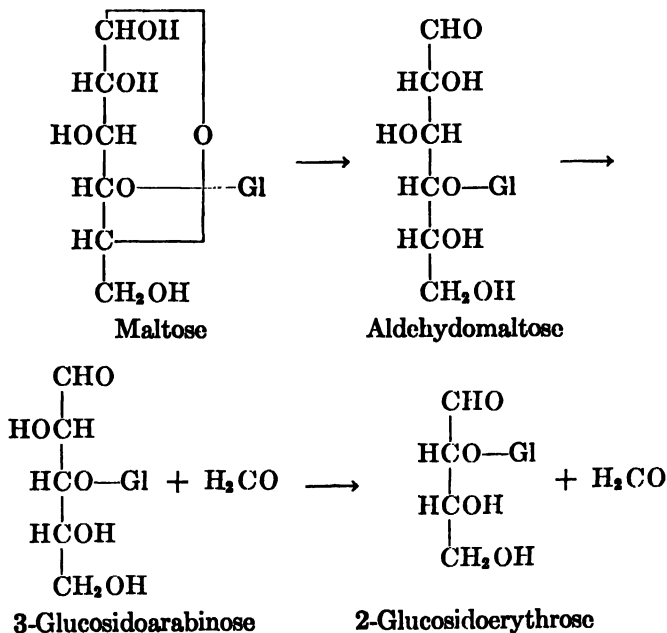
in alkalies as it does in acids.   Since this was not the case, the reaction of maltose in an alkaline solution must be explained by some other mechanism.

For this purpose it has been assumed that maltose may undergo a fragmentation in two different reactions until 2-glucosidoerythrose is reached, as shown on page 555.   Then it may be assumed that 2-glucoscidoerythrose may undergo hydrolysis as follows:

$$
\begin{array}{lll}
\text{CHO} & \text{CH}_2\text{OH} & \text{CH}_2\text{OH} \\
| & | & | \\
\text{HCO}\!-\!\text{Gl} & \text{CO}\!-\!\text{Gl} + \text{HOH} & \text{COH} + \text{Glucose} \\
| \quad\longrightarrow & | \quad\longrightarrow & \| \\
\text{HCOH} & \text{COH} & \text{COH} \\
| & | & | \\
\text{CH}_2\text{OH} & \text{CH}_2\text{OH} & \text{CH}_2\text{OH}
\end{array}
$$

2-Glucosidoerythrose   2-Glucosidoerythrose   Erythrose 2,3-enediol
                                          2,3-enediol
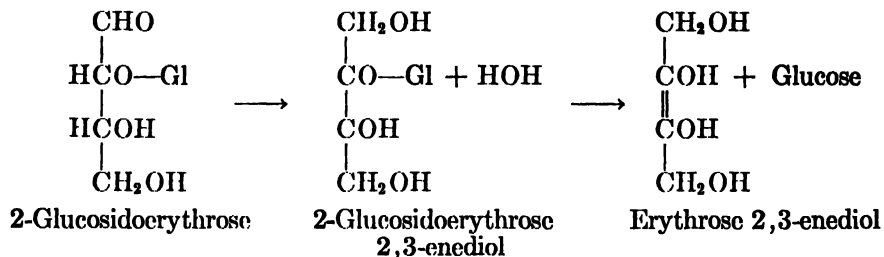
Summarizing, the theory set forth here may be expressed in the following word equations:

(1)   Maltose→ 3-Glucosidoarabinose + Formaldehyde

(2)   3-Glucosidoarabinose→ 2-Glucosidoerythrose + Formaldehyde

(3)   2-Glucosidoerythrose + Water→ Erythrose + Glucose

_____

Maltose + Water = Glucose + Erythrose + Formaldehyde + Formaldehyde
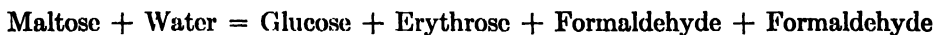
The following is a second possibility:

(1)   Maltose → 2-Glucosidoerythrose + Glycolaldehyde

(2)   2-Glucosidoerythrose + Water → Glucose + Erythrose

_____

Maltose + Water → Glucose + Erythrose + Glycolaldehyde
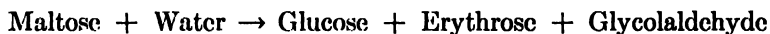
An examination of the fragmentation and hydrolytic products of these changes reveals that only one of the original two molecules of glucose composing maltose is obtained unchanged; hence only one-half the amount of lactic acid could have been expected, since the other reaction products do not yield lactic acid under the same experimental conditions, save for the possible formation of formose from formaldehyde in the presence of alkalies.   If this occurs under these conditions, the quantitative experimental data obtained from maltose are best understood from the second possibility, because glycolaldehyde and erythrose do not form lactic acid in the presence of alkalies.

These postulates need experimental verification: i.e., it must be shown that alkaline hydrolysis is actually involved in these reactions, and that the reducing section of the maltose molecule is not producing lactic acid.   A number of experiments have been carried to completion, and the data obtained have been in harmony with the views expressed above.

If the data with reference to the relative yields of lactic acid obtained from 0.5 M glucose and 0.25 M maltose solutions are correct, then it follows that if the lactic acid yields from alkaline solutions of 0.5 M maltose are compared with those of 0.5 M glucose, the curve expressing the yields of lactic acid as a function of the alkali normality should tend to become identical with that obtained with 0.5 M glucose. This was found to be true.

To test these assumptions still further, the following pairs of oligosaccharides were synthesized for the first time: glucosidodihydroxyacetone pentaacetate (22) and cellobiosidohydroxyacetone octaacetate; galactosidodihydroxyacetone pentaacetate and lactosidodihydroxyacetone octaacetate. The two components of the glucosidodihydroxyacetone pentaacetate are the terminal ones in the cellobiosidodihydroxyacetone octaacetate molecule in which they are both combined to a central glucose molecule. The same relationship is true for the galactosidodihydroxyacetone pentaacetate and the lactosidodihydroxyacetone octaacetate molecule with glucose, as above, also being the central molecule in the latter pair of compounds. In harmony with the views expressed above, the central glucose constituent in the two new trisaccharides will be prevented from giving any glucose by reason of the fragmentation reaction yielding a tetrose molecule in each case, and hence there is left for lactic acid formation only the dihydroxyacetone portion of each trisaccharidic molecule plus the glucose and galactose united at C_4 of the central glucose component. Therefore, it follows that the yields of lactic acid obtained from the glucose dihydroxyacetone pentaacetate and cellobiosidodihydroxyacetone octaacetate should be approximately the same, and those obtained from the galactosidodihydroxyacetone pentaacetate and lactosidodihydroxyacetate octaacetate should likewise be approximately equal to each other. This was found to be true in each case. Had the central glucose portion of the cellobiosidic and lactosidic derivatives reacted in alkaline solutions to give lactic acid, then this relationship would not be true.

To search for further support of the above postulates, an experimental study was next made on the behavior of Helferichs 6-cellobiosido-D-glucose hendecaacetate and a newly synthesized 6-maltosido-D-glucose hendecaacetate (44), in alkaline solution. On the basis of the views set forth above, the lactic acid obtained from these trisaccharides should approach as a limiting value that which may be obtained from a mixture of two molecular equivalents of glucose in the presence of eleven molecular equivalents of potassium acetate; i.e., the central glucose molecule in each of the two trisaccharides should not yield any lactic acid. This relationship was found to be true. The predictions which were made with reference to the relative yields of lactic acid obtained from the newly synthesized 6-cellobiosidomannose (44) and 6-maltosidomannose (44) in alkaline solutions as tending towards the yields of lactic acid obtained from mixtures of one mole equivalent each of mannose and glucose were verified.

The above experimental data immediately suggested that a comparative experimental study should be made of the yields of lactic acid which would be obtained from 6-gentiobiosidoglucose hendecaacetate and 6-cellobiosidoglucose hendecaacetate, for the reason that in the former case there should be no in-

hibitory action in the central glucose molecule (section B, below) while there
would be such an inhibitory effect in section B of the latter.
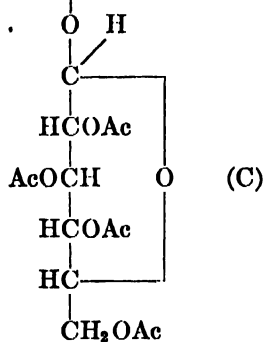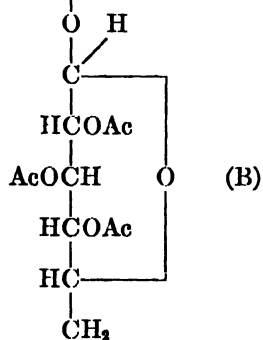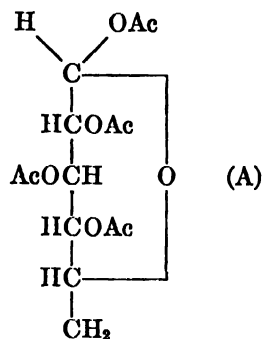
6-Gentiobiosidoglucose   6-Cellobiosidoglucose hendecaacetate
  hendecaacetate
  (A = gluose, B = glucose, C = glucose)
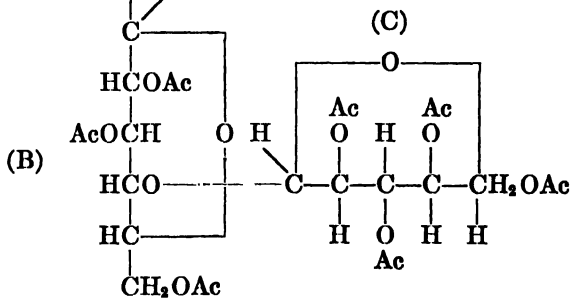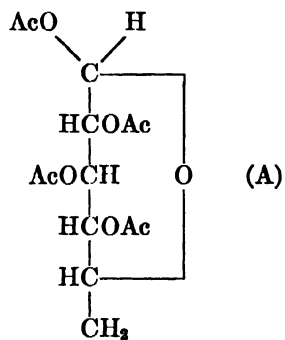
The experimental data confirmed this point of view, as did also the results of a
comparative study made on the newly synthesized 6-melibiosidoglucose hendeca-
acetate and 6-lactosidoglucose hendecaacetate.

If the above reasoning is applied to cellulose, in which each glucose unit, save
one, is laden at carbon atom 4 with another glucose unit, then it would appear

that only one of the glucose units of the cellulose molecule would yield lactic acid. Under such circumstances, it would also be necessary to conduct the experiment in the absence of atmospheric oxygen. The glucose unit which should yield lactic acid is the one which is not laden at carbon atom 4 with another glucose unit, i.e., it is at the extreme end of the chain of glucose units composing the cellulose molecule, while the one reducing glucose unit is at the opposite end. The insolubility of the cellulose and its dispersion to the molecular condition make the experimental realization of these statements very difficult.

Finally, the main purpose in this discussion has been to trace the development of an area in carbohydrate chemistry which is full of fundamental interest. Although the chemical theory of the carbohydrates has been largely developed by the use of relatively few sugars, such as arabinose, glucose, mannose, fructose, galactose, maltose, lactose, sucrose, the starches, and cellulose, yet a beginning has only been made. In addition to the many synthetic opportunities, improvements in older methods, development of new methods, and searching for new sources of the more rare sugars among the plants, there is a great opportunity for quantitative work in a study of the molecular life history of the many reactions of the carbohydrates in these days when the electonic conception of the nature of chemical change is playing such an important rôle. It is at this point where the organic chemist, the biochemist, and the physical chemist can join hands with much profit. All the modern tools of investigation, as well as a full consideration of the physical-chemical aspects of our problems, will greatly aid in a richer development of this important field of organic chemistry.

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EXPERIMENTAL FACTS PERTAINING TO THE RELATIONSHIP BETWEEN VISCOSITY, MOLECULAR SIZE, AND MOLECULAR SHAPE[1]

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I. INTRODUCTION

Until about ten or twelve years ago, few people thought of interpreting the viscosity increment imparted to a solvent by a solute as being related in any way to the size and shape of the solute particles. Most thinking was dominated by the Einstein equation (12),

$$\frac{\eta}{\eta_0} - 1 = 2.5G \tag{1}$$

where $\eta/\eta_0 - 1$ is the specific viscosity and G is the volume fraction of the solute. According to this equation, the viscosity of a solution or suspension of large spheres is related in no way whatever to the size of the spheres but only to the total volume concentration. It was early recognized that the viscosities of most solutions and suspensions were much too high to be accounted for by the Einstein equation. The usual explanation was that the particles soaked up solvent and occupied more space in solution than in the dry state. It became fashionable to calculate the specific hydrodynamic volume of a colloid from its viscosity, using the Einstein equation, and to regard the ratio of this term to the true specific volume in the dry state as a measure of the degree of solvation of the particles. Table 1, assembled by Kraemer (33) in 1931, shows the ratios of specific hydrodynamic volumes, Φ, calculated from viscosity measurements, to true specific volumes, V, for several colloidal materials. On the basis of the foregoing, it is evident from a consideration of the data in this table that there are two kinds of colloids,—those in which the ratio is near unity and those in which it is considerably greater than unity. The members of the first group were thought to be lyophobic colloids and those of the second, lyophilic colloids. In several instances the specific hydrodynamic volumes of members of the second group may be seen to be several hundred times the true specific volumes. The absurdity of attempting to explain a situation of this sort simply in terms of solvation was beginning to be generally recognized about the time these data were assembled, and Kraemer reflected this trend by suggesting that unusually high viscosities might be caused "by greatly elongated particles or macromolecules that increase resistance to shear through mutual entanglements and interference, but without ordinary flocculation." Here may be seen the germ

of the notion that there is some connection between the size or shape of a particle and the viscosity of its solution. It is the purpose of the present review to assemble the principal experimental facts upon which this idea rests at the present time. Several excellent, though somewhat less inclusive, considerations of the same general topic are available in the literature (49, 50, 53, 58, 70). The treatment can be divided into two definite sections: First, there will be an examination of those data in the literature from which some sort of a connection between particle size or shape and viscosity can be established on a purely empirical basis. Second, some of the attempts which have been made on theoretical grounds to explain the alleged relationship between viscosity and molecular size and shape will be examined in the light of pertinent experimental findings.

TABLE 1

Ratios of specific hydrodynamic volume to true specific volume for various colloids (33)

COLLOID	Φ/V	COLLOID	Φ/V
Sucrose in water..........	1.6	Clay in water.........................	9
		Starch in water.......................	20
		Gum arabic in water..................	50
Egg albumin in water......	0.9	Agar in water at 50°C.................	220
		Isoelectric gelatin at 40°C............	6
		Isoelectric gelatin at 20°C............	30
Sulfur in water............	1.2	Nitrocellulose in ethyl acetate.........	80
Gamboge in water.........	1.25	Cellulose acetate in acetone...........	200
		Polyvinyl acetate in benzene..........	200–900
Diluted rubber latex.......	1.00	Rubber in benzene....................	300–500
		Polystyrene in benzene...............	4–1000

II. EMPIRICAL APPROACH

A. Linear compounds and polymers

Owing to the pioneering work of Staudinger and his collaborators (73) and to the challenge presented by their findings, an extensive literature is available on the relationship of the viscosity of chain-type compounds and polymers to their molecular weights. In this review, an attempt has been made to sort from the literature those studies in which viscosity and independent molecular-weight measurements of apparently high reliability were carried out on the same preparations of several members of homologous or polymer series of well-defined substances. The materials range in size from the simpler straight-chain paraffin molecules to macromolecular polymers and natural products. The molecular weights of the simpler compounds considered here were determined by the usual procedures of the structural chemist. One or more of three general methods were used for determining the molecular weights of the more complex molecules: (*1*) end-group titrations, (*2*) vapor-pressure, osmotic, and cryoscopic studies, and (*3*) ultracentrifugation-equilibrium measurements. In the case

of vapor-pressure and related methods, rather serious difficulties attend the extrapolations to zero concentration, necessary in the case of linear macromolecules. For that reason, in this review only qualitative significance is attached to those studies in which these methods were the only ones available for the independent determination of the molecular weight. In all of the studies considered, viscosities were computed from measurements of the rate of flow through a capillary tube.

In the subsequent considerations, the viscosity of the pure solvent at a given temperature will be represented by the symbol η_0, and that of the solution at the same temperature by the symbol η. Then η/η_0 will be defined as the relative viscosity, η_r, of the solution and $(\eta - \eta_0)/\eta_0$ or $\eta/\eta_0 - 1$ as the specific viscosity, η_{sp}. It is a matter of common experience that the specific viscosity is a function
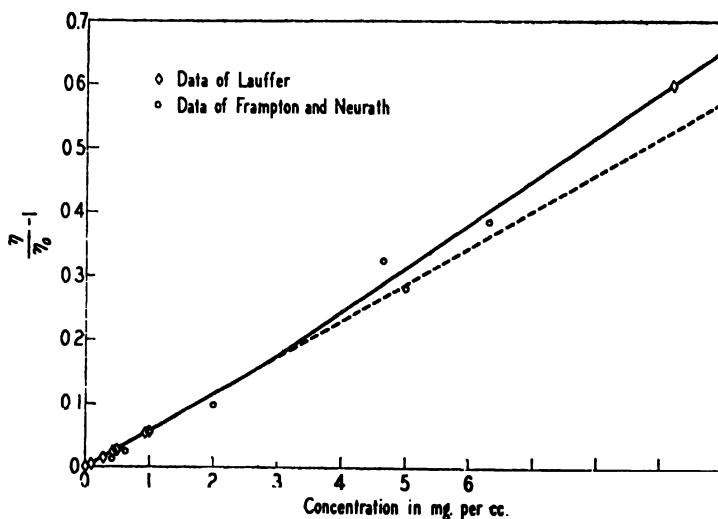
FIG 1. Specific viscosity of tobacco mosaic virus nucleoprotein plotted as a function of concentration in milligrams per cubic centimeter. From Lauffer and Stanley ((47).)

of the volume concentration of the solute. As is illustrated by the data in figure 1, in very dilute systems this function is linear (25, 44). Hence, the mathematical quantity which characterizes any given substance is the expression η_{sp}/G. With most substances, specific viscosity is a linear function of concentration only in rather dilute solutions. It is necessary, therefore, to use the limiting value of the expression η_{sp}/G as G approaches zero. Following Kraemer's suggestion (34), this function will be called "intrinsic viscosity."[2] There are three general

---

[2] Kraemer (34) uses the term "intrinsic viscosity" symbolized by $[\eta]$, to define the limiting value of the ratio, η_{sp}/c, for the special case in which c is expressed as grams of solute per 100 cc. of solution. The symbol $[\eta]_v$ is used to represent the analogous function for the case in which concentration is expressed as cubic centimeters of solute per 100 cc. of solution. Since there are many different manners of expressing concentrations in viscosity studies, in this review the term "intrinsic viscosity" will be used to define the limit of η_{sp}/c or η_{sp}/G without restriction to the mode of describing concentration. In each case, the units

methods of evaluating the limit of η_{sp}/G from experimental data. The simplest of the three is to plot specific viscosity as a function of concentration and then to draw a tangent to the experimental curve at the point represented by zero concentration. This procedure was used in the very favorable case of tobacco mosaic virus illustrated in figure 1. The second method is based upon the empirical relationship observed by Arrhenius (2) to apply over a considerable concentration range: $\log \eta_r = kG$, where k is a proportionality factor. On the
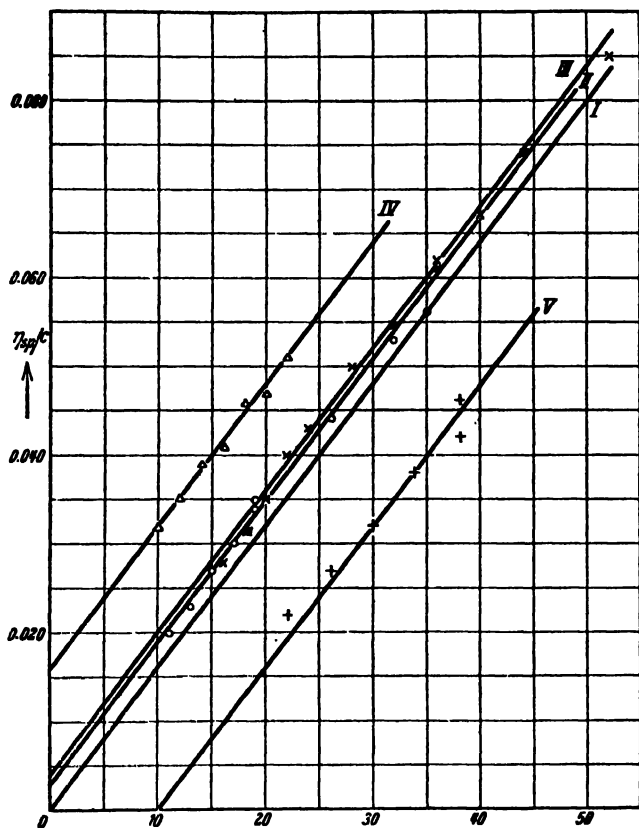
FIG. 2. Base molar intrinsic viscosities of chain molecules (ordinate) plotted as functions of numbers of carbon atoms in chain (abscissa). Curve I, normal paraffins; curve II, normal fatty acid esters; curve III, normal fatty acids; curve IV, normal fatty acids in pyridine; curve V, normal alcohols. (From Staudinger (73).)

basis of this relationship, $\log \eta_r$ is plotted against G and $\log \eta_r/G$ is evaluated. When natural logarithms are used, the fraction, $\log \eta_r/G$, is equal to the limit of η_{sp}/G or $[\eta]$, because $\log \eta_r$ is approximately equal to $\eta_r - 1$ or η_{sp}, when η_{sp}

of the concentration term will be stated. In some of the studies discussed, it is doubtful that the limiting values of the ratio have been determined. However, most of the measurements in such cases were made on quite dilute systems, so that the ratios presented may be regarded as reasonable approximations of the intrinsic viscosity.

is very small. The third method of getting the limiting slope depends upon the observation that a power series, $\eta_{sp} = AG + BG^2 + CG^3 + \cdots$, can describe the viscosity–concentration function over a wide concentration range (5). The constants A, B, C, etc., are evaluated from the data by any one of several accepted methods. Since all higher powers of G become insignificant compared to G when G approaches zero, the value of A is the limiting value of η_{sp}/G. Any one of the above three treatments when applied to suitable data should yield a reasonable approximation of the intrinsic viscosity.

In figure 2 are presented some of the data of Staudinger and Ochiai (73, 74, 77) on the viscosity of homologous series of fairly simple, chain-type organic compounds of known molecular weight. Intrinsic viscosity is plotted against
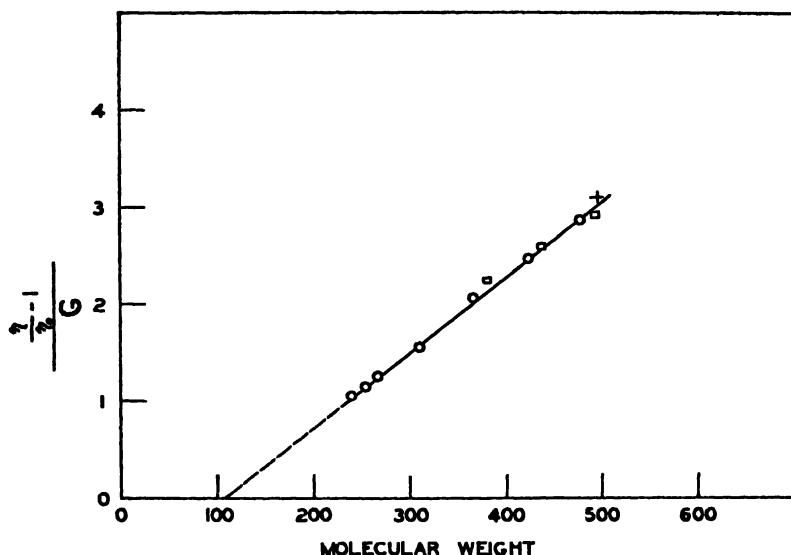
Fig. 3. Volume fraction intrinsic viscosities of normal hydrocarbons plotted against molecular weight. O, data of Meyer and van der Wyk (54); □, data of Staudinger and Staiger (79); ×, datum of Staudinger and Ochiai (77).

number of carbon atoms in the chain. Staudinger expressed concentrations in terms of the molarity of the basic repeat unit, the CH_2 group in these examples. If these intrinsic viscosities are recalculated on the basis of volume fractions, a new scale of ordinates must be applied to figure 2. Unity on the new scale would coincide with about 0.018 on the old, and 2.5, the coefficient in the Einstein equation for spheres, would fall between 0.04 and 0.045 on the old. This means that the intrinsic viscosities of at least half of the linear molecules represented in this study are less than that predicted for large spheres by the Einstein equation.

Meyer and van der Wyk (54) investigated in a most painstaking manner the viscosities of carbon tetrachloride solutions of normal paraffin hydrocarbons with chain lengths between seventeen and thirty-four carbon atoms. Data

were obtained for similar systems by Staudinger and Staiger (79). The intrinsic viscosities calculated on the basis of volume fractions from the data of these two investigations are plotted as a function of molecular weight in figure 3.

The viscosities of essentially monodisperse polyoxyethylene glycol preparations dissolved in carbon tetrachloride and in dioxane were studied by Fordyce and Hibbert (23). These compounds were synthesized by Fordyce, Lovell, and Hibbert (24) according to the reaction:

$$ClCH_2CH_2O[CH_2CH_2O]_xCH_2CH_2Cl + 2KOCH_2CH_2O[CH_2CH_2O]_yCH_2CH_2OH$$

$$\rightarrow HOCH_2CH_2O[CH_2CH_2O]_{(x+2y)}CH_2CH_2OH + 2KCl$$
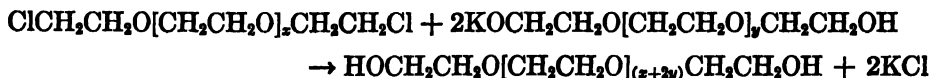
This should lead to essentially monodisperse compounds of known structure and molecular weight. In figure 4 the data for the intrinsic viscosities of various
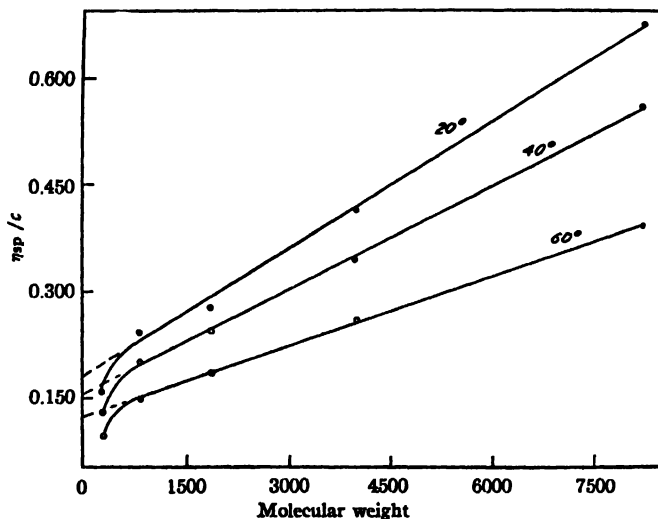
Fig. 4. Base molar intrinsic viscosities at various temperatures of polyoxyethylene glycols in carbon tetrachloride plotted against molecular weight. (From Fordyce and Hibbert (23).)

polyoxyethylene glycols in carbon tetrachloride are plotted as a function of molecular weight. The concentrations are expressed in terms of base molarity, where the [CH_2CH_2O] group represents the repeat unit. If these concentrations had been expressed in terms of the volume fraction, 2.50 on the scale of ordinates would have come close to 0.150 on the present scale. If the data obtained with dioxane as a solvent are plotted in a similar manner, comparable curves are obtained, differing chiefly in having somewhat greater slopes.

Flory and Stickney (22) measured the viscosity of various preparations of decamethylene adipate polymers dissolved in diethyl succinate and in chlorobenzene. These polymers were obtained by allowing equimolar proportions of decamethylene glycol and adipic acid to react to various extents. All of the preparations thus obtained were composed of particles of many sizes. The
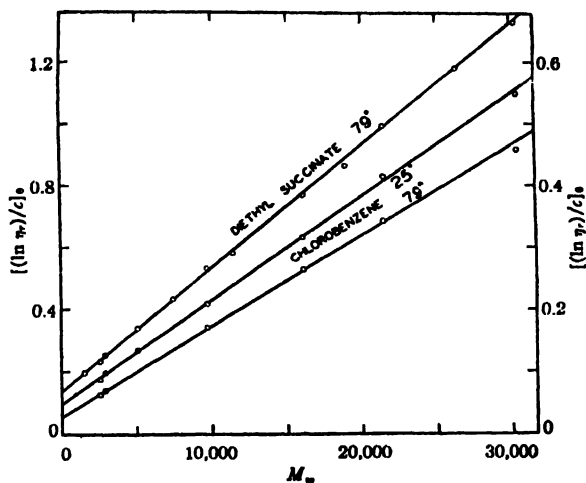
FIG. 5. Base molar intrinsic viscosities of decamethylene adipate polymers in chlorobenzene at 25° and 79°C. (right-hand scale of ordinates) and in diethyl succinate at 79°C. (left-hand scale of ordinates) plotted against weight average molecular weights. (From Flory and Stickney (22).)

weight average[3] molecular weight of each preparation was determined from measurements of the viscosity of the molten polymer.[4]   In figure 5, the intrinsic

[3] In studies on the size and related properties of inhomogeneous materials, it is necessary to distinguish between several different types of averages.   The number average molecular weight is simply the total weight of material divided by the total number of moles of particles present.   The weight average molecular weight is the limiting value, as the number of fractions approaches infinity, of the average of the molecular weights of the very small practically monodisperse fractions of equal bulk into which the total mass of the material can be divided.   The number average molecular weight attaches equal significance to very large and very small molecules.   The weight average molecular weight attaches equal significance to equal weights of very small and very large molecules.   In a very heterogeneous system, the number average molecular weight can be very much smaller than the weight average molecular weight.   Kraemer and Lansing (39) pointed out, and Lovell and Hibbert (48) and Baker, Fuller, and Heiss (4) demonstrated experimentally, that the intrinsic viscosity of a polydisperse material is a function of the weight average molecular weight and not of the number average molecular weight.

[4] Flory (21) has shown that there is a linear relationship between the logarithm of the melt viscosity of polyester preparations and the square root of the weight average molecular weight.   In establishing this relationship, melt viscosities and number average molecular weights obtained by end-group titrations were measured on various polyester preparations. Weight average molecular weights were calculated from the number average molecular weights on the basis of a theoretical distribution function previously derived (19), and then these values were used in connection with the viscosity data to establish the relationship in question.   In view of this, the weight average molecular weight determinations of Flory and Stickney depend ultimately upon end-group titrations and upon the validity of Flory's distribution theory.   The introduction of this theoretical consideration destroys somewhat the empiricism of the approach to the relationship between the intrinsic viscosity and the weight average molecular weight of the polyesters.   However, Flory's distribution function was derived by straightforward statistical considerations on the basis of the

viscosities of decamethylene adipate polymers are plotted as a function of the weight average molecular weight. Intrinsic viscosities were computed on the basis of concentration expressed in terms of base molarity, the repeat unit being considered to be something a little bigger than a methylene group. The right-hand scale of ordinates applies to the polyester dissolved in chlorobenzene and the left-hand scale to the polymer dissolved in diethyl succinate. Had concentrations been calculated as volume fractions, the value of the ordinate 2.5 would coincide approximately with 0.08 on the present scale.

The polyesters just discussed cover about the same molecular weight range as the ω-hydroxydecanoic acid polymers prepared by Carothers and van Natta (8) and studied in the viscometer by Kraemer and van Natta (41). Number average molecular weights were determined by means of an end-group titration. Since these polymers were fractionated by crystallization, even now that a distribution theory (19) is available, it is not possible to convert number average molecular weights into weight average molecular weights. Sedimentation-equilibrium measurements made by Kraemer and Lansing (37) on the largest polymer of the series did, however, yield a value for the average molecular weight—presumably the weight average—not too different from the value obtained by titration. All in all, this study represents a very important contribution, because it first clearly demonstrated that the relationship between the molecular weight and the intrinsic viscosity of polymeric materials is one of approximate linearity rather than direct proportionality.

More recently Baker, Fuller, and Heiss (3) studied the viscosity of polymer preparations obtained by allowing pure ω-hydroxyundecanoic acid to polymerize at 200°C. Number average molecular weights were determined by means of titration with alcoholic sodium hydroxide. From Flory's distribution theory (19) it can be determined that the weight average molecular weight is approximately equal to 1.94 times the number average molecular weight for all of the polymer preparations considered in the above work. On this basis, weight average molecular weights were computed from the data presented in the publication. Viscosities were measured in reagent-grade chloroform. In figure 6, intrinsic viscosity is plotted as a function of weight average molecular weight. The concentration term involved in the evaluation of the intrinsic viscosity was expressed in volume fractions. A more or less comparable study has been carried out by Staudinger and Nuss (76). From a gross point of view, the data obtained by these workers are in agreement with those presented in figure 6. However, Staudinger and Nuss regard their results as a confirmation

assumption that the reactivity of the end groups does not change as the polymers increase in size. Kinetic studies demonstrated the substantial validity of this assumption (20). Hence, the theory can be considered to be established experimentally, at least in part. The distribution theory provides that the weight average–number average molecular weight ratio is approximately a constant for all preparations of the polymer considered by Flory and Stickney. Hence, if the number average molecular weights of the polyester, which can be obtained entirely experimentally, were plotted against intrinsic viscosity, linear relationships similar to those of figure 5, but differing in slope, would be obtained.

of the Staudinger rule of direct proportionality between intrinsic viscosity and molecular weight. In order to evaluate the conflicting interpretations, it is necessary to observe that the data of the latter workers do not seem to possess quite the same degree of internal consistency as those of Baker, Fuller, and Heiss.

There has long been a discussion as to whether or not a simple relationship of viscosity to molecular size obtains for the true macromolecules,—particles with molecular weights up to half a million. Staudinger (75) has assembled some data on polystyrene. Styrene was allowed to polymerize at each of several temperatures, and then each batch was fractionated. The number average molecular weight of each fraction was determined by osmotic-pressure measurements and the intrinsic viscosity of each fraction dissolved in toluene
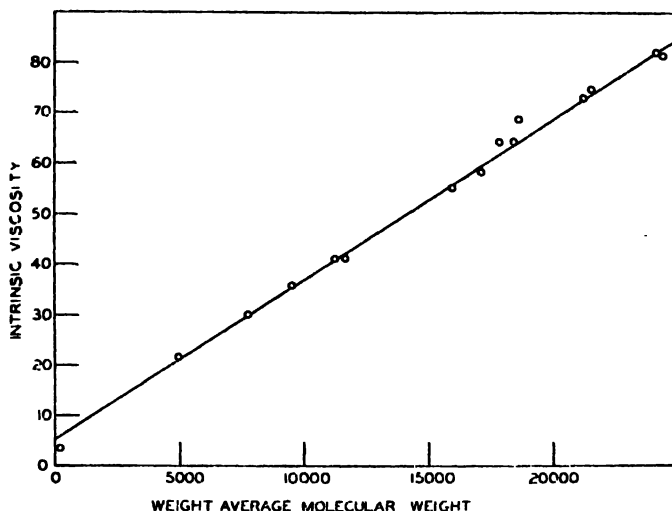
FIG. 6. Volume fraction intrinsic viscosity of ω-hydroxyundecanoic acid self-polymers in chloroform plotted against weight average molecular weight. (Data of Baker, Fuller, and Heiss (3).)

was measured. The results show approximately linear relationships between the intrinsic viscosities and the number average molecular weights of the fractions of each batch, but both the slopes and the intercepts of the lines vary from batch to batch. Signer and Gross (64, 65, 66) measured the molecular weights of some polystyrene fractions by means of sedimentation equilibrium. Sufficiently dilute solutions were studied so that the extrapolation hazards involved in osmotic measurements could be avoided. Viscosities of the same materials dissolved in chloroform were obtained. These results demonstrated an approximate proportionality between intrinsic viscosity and molecular weight.

Staudinger (75) has also assembled data on the intrinsic viscosities and the osmotically determined number average molecular weights of various nitrocellulose preparations dissolved in acetone, of various degraded methyl celluloses

dissolved in water, and of various polyethylene oxides dissolved in water. Later, Staudinger and Reinecke (78) presented data on the viscosities of various fractions of ethyl cellulose, ethyl acetyl cellulose, methyl cellulose, and methyl acetyl cellulose. Here too, molecular weights were estimated osmotically. All of these studies indicated approximate proportionality between the number average molecular weights and the intrinsic viscosities for each type of material.

Kraemer and his associates made extended studies of the viscosities and molecular weights of a great many degradation products of natural polymers. They measured molecular weights by the sedimentation-equilibrium method,
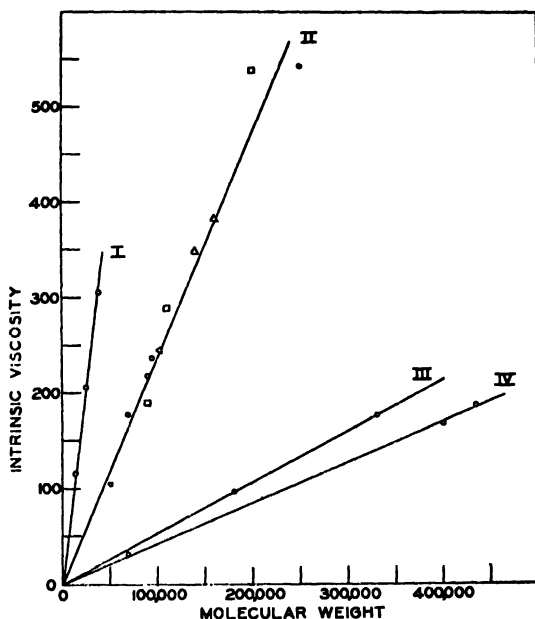
FIG. 7. Volume fraction intrinsic viscosities of various natural and synthetic polymers plotted against weight average molecular weights. Curve IV, rubber in ether (Kraemer and Nichols (40)). Curve III, polychloroprene in n-butyl chloride (Kraemer and Nichols (40)). Curve II: □, cellulose in cuprammonium; ○, cellulose acetate in acetone; △, nitrocellulose in acetone (Kraemer (34)). Curve I, methyl cellulose in water (Signer (65, 67, 68)).

carrying out the calculations (43) in such a manner as to obtain weight average molecular weights. In figure 7, curve II, the weight average molecular weights of various polydisperse cellulose and cellulose derivative systems (34, 38, 39, 40) are plotted against intrinsic viscosities calculated on the basis of volume fractions. Signer and collaborators (65, 67, 68) carried out an analogous study on methyl cellulose fractions dissolved in water. Their data, calculated in the same manner as in the preceding case, are presented in figure 7, curve I. In a comparable manner, Kraemer and associates (40) studied rubber fractions in ether and polychloroprene in n-butyl chloride. The results of these studies, computed as described above, are presented in curves III and IV of figure 7.

Kemp and Peters (32) have recently considered the intrinsic viscosities of numerous rubber degradation fractions dissolved in benzene and in hexane in relation to the average molecular weights determined cryoscopically. Extrapolated values of the molecular weight showed an approximately linear relationship to intrinsic viscosity.

When all of the data that have just been presented on linear molecules and linear polymers are considered, four important facts are outstanding: (1) It is clear that for all of the cases examined, including the very simplest chain molecules, the largest macromolecular structures, and all intermediates, the intrinsic viscosities can be expressed at least approximately as linear functions of molecular weights or chain lengths, according to equations of the form,

$$[\eta] = \beta + KM \tag{2}$$

where M represents the molecular weight. (2) The data show that the constants β and K can vary considerably from system to system. The variability in β is evident from a consideration of the data of Staudinger and Ochiai (77) on simple chain molecules, presented in figure 2. From these same data, however, one might be led to expect that the value of K is a general constant applicable for a given solvent to all molecules which have the carbon atom as a recurring unit. In conformity with this idea, Staudinger (73, 74) represented the viscosity-molecular weight relationship of the normal hydrocarbons by a line drawn parallel to the other lines of figure 2, through the origin and through a single datum. However, the graph of the relationship between intrinsic viscosity and the molecular weight of the normal hydrocarbons representing the results of the more extended and more exacting study of Meyer and van der Wyk (54) may be seen in figure 3 not to extrapolate to the origin. Since the data of Staudinger and Ochiai (77) and of Staudinger and Staiger (79) fit this graph fairly well, this means that the slope of the hydrocarbon graph is actually not quite the same as that of the other systems represented in figure 2. Hence, K must be regarded as a specific rather than a general constant. (3) These data show that, within a given homologous or polymeric series, the intrinsic viscosity-molecular weight relationship varies from solvent to solvent and from temperature to temperature. The studies of Flory and Stickney (22), of Fordyce and Hibbert (23), and of Kraemer and van Natta (41) bring out the facts that both the intercepts and the slopes of the graphs may be varied by changing solvents and by changing the temperature. (4) As was pointed out previously, several of the various studies here considered show that it is possible for chain molecules to have lower intrinsic viscosities than that predicted by Einstein for large spheres. The significance of this point will be discussed later in connection with a consideration of the theoretical aspects of the question.

It appears, then, on the basis of a wealth of reasonably good measurements of the intrinsic viscosities of simple chain-type molecules and of chain-type polymers with well-characterized molecular weights, that a linear relationship between intrinsic viscosity and molecular weight exists for each homologous or

polymeric series.[5] This is valid for systems ranging in size from the simplest small molecules to the macromolecular polymers. The constants characterizing these relationships vary not only from series to series, but from solvent to solvent and from temperature to temperature within a given series. From the practical point of view, these facts mean that the very simple viscosity technique can be adapted to the measurement of the molecular weight of chain-type compounds or polymers, but only after the method has been standardized by an independent and reliable procedure for each series of molecules or particles in a given solvent at a given temperature. An illustration of such a use of viscosity data was recently afforded by Mead and Fuoss (50a). From a theoretical point of view, a relationship of such a degree of generality as that here obtained suggests strongly that there is actually some fundamental connection between the size of a chain-type molecule and its solution viscosity. However, that hypothetical relationship must be one in which several other factors play a significant part.

B. Proteins

Many protein solutions are known to have intrinsic viscosities far greater than that predicted for spheres by the Einstein equation. In view of the relationship between viscosity and molecular weight established for linear polymers, it is natural to inquire whether such a relationship exists for proteins also. If intrinsic viscosities are plotted against molecular weights for the many proteins which have been investigated, no correlation of any significance is observed. However, if the intrinsic viscosities of these same proteins are plotted against the molecular shape as determined independently, a very real correlation may be obtained. This is illustrated in figure 8, where the volume fraction intrinsic viscosities of several proteins and related materials are plotted against the axial ratios of the rod-shaped ellipsoids of revolution assumed to represent the protein particles.[6] It may be observed that all of these intrinsic viscosities exceed the Einstein value for large spheres.

[5] Staudinger draws a slightly different conclusion from many of the same data that have been considered here. He insists that the intrinsic viscosity is directly proportional to the molecular weight of linear macromolecules,—in other words, the constant β of equation 2 is 0. For those systems in which a graph of intrinsic viscosity *versus* molecular weight fails to extrapolate to the origin, Staudinger believes that the lower members of the series are associated or aggregated and that the viscosity studies can be used to measure the extent of association. K. H. Meyer has recently reviewed much of the literature pertaining to this issue and has concluded that the Staudinger law of direct proportionality does not adequately describe the relationship between viscosity and molecular weight (53). Very recently Flory (21a) reported that the intrinsic viscosity of polybutene is accurately proportional to the 0.606th power of the osmotically determined molecular weight within the range from 5000 to 500,000. Not only is this result at variance with the views of Staudinger, but also it constitutes an exception to the rather general approximately linear dependence of intrinsic viscosity upon the molecular weight of chain-type polymers.

[6] Kraemer (35, 36) has carried out viscosity, sedimentation, and diffusion studies on gelatin in various non-gelating solvents. If his value for intrinsic viscosity were plotted against the axial ratio calculated from the sedimentation and diffusion data, the point would

The data here presented were obtained or assembled by Polson (62), by Neurath and associates (55, 56), by Carter and Hall (9, 10), and by workers at the Rockefeller Institute (11, 45). The materials represented are egg albumin, serum albumin, hemoglobin, amandin, gliadin, serum globulin, thyroglobulin, *Octopus*, *Homarus*, and *Helix* hemocyanins, pepsin, lactoglobulin, thymus nucleohistone, tobacco mosaic virus, and tobacco mosaic virus nucleic acid. The axial ratios here shown were calculated, for the most part, from diffusion, sedimenta-
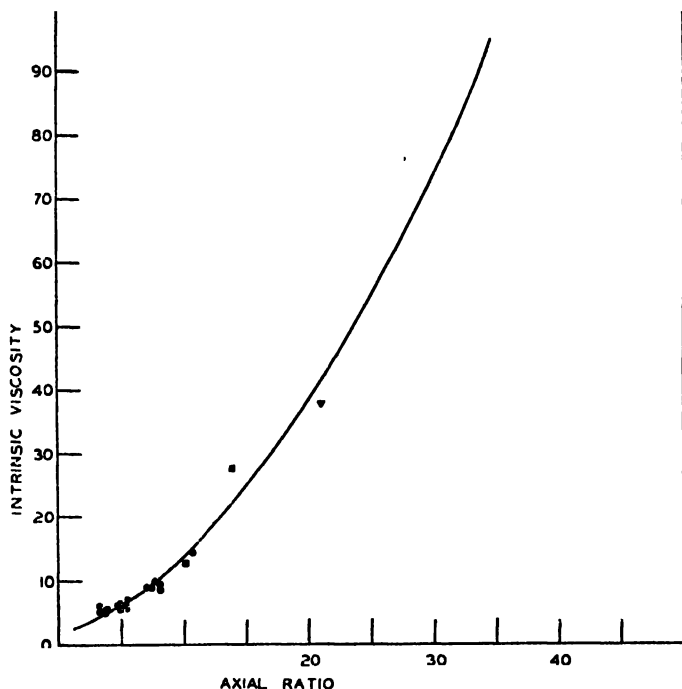
Fig. 8. Volume fraction intrinsic viscosities of various proteins and protein derivatives plotted against axial ratios obtained from independent data for the case of rod-like shape. ●, data of Polson (62) and of Neurath (55, 56); ○, thymus nucleohistone (9, 10); ▼, tobacco mosaic virus (45); ■, tobacco mosaic virus nucleic acid (11).

tion, and specific-volume data.[7] The molecular weight of the protein was first computed by use of the equation

fall far to the right of those shown in figure 8. This may be due to the difficulties which, as Kraemer emphasized, are experienced in this case in extrapolating diffusion data to zero concentration.

[7] The axial ratios of the two tobacco mosaic virus preparations (▼ in figure 8) were determined by measuring the particle lengths from electron micrographs, by computing the weight average length (forty or more particles), and by then dividing this by the particle thickness established by x-ray studies. The absolute error in these values is probably less than 10 per cent. Viscosities were measured in a capillary viscometer. The preparation having the lower intrinsic viscosity gave a single boundary in the ultracentrifuge and a unimodal distribution of particle lengths in the electron micrograph (45). Its viscosity is of the same order of magnitude as that reported previously by Stanley (71). The prepara-

$$M = \frac{RTS}{D(1 - V\rho)} \tag{3}$$

R is the gas constant, T the absolute temperature, S the sedimentation constant, D the diffusion constant, V the partial specific volume of the protein, ρ the density of the solution, and M the molecular weight (81). From the molecular weight and partial specific volume, the radius of a sphere having the same weight as each particle was next calculated. Then, by use of the Einstein–Sutherland (13, 80) equation,

$$D = \frac{RT}{6\pi\eta_0 rN} \tag{4}$$

where r is the radius and N is Avogadro's number, the value, D_0, that the diffusion constant would have if the particles were spheres of specific volume V was computed. The real measured diffusion constant was next divided by this artificial or ideal diffusion constant to get the quotient D/D_0. When this quotient is unity, it is justifiable to conclude that the protein molecules under question are really spheres with specific volume V. In the cases of all of the proteins involved in these considerations, the ratios were less than unity. There are three possible interpretations of such a situation: (1) The protein molecules might be rods instead of spheres. A relationship has been derived (26, 28, 60) between D/D_0 and b/a for elongated ellipsoids of revolution which can be expressed as follows when $b/a \gg 1$:

$$\frac{D}{D_0} = \frac{(a/b)^{2/3}}{\sqrt{1 - (a/b)^2}} \ln\left(\frac{1 + \sqrt{1 - (a/b)^2}}{a/b}\right) \tag{5}$$

where a is the minor and b the major axis. Hence, when D/D_0 is known, a/b can be evaluated. (2) The protein particles might be plate-like ellipsoids of revolution. A relationship comparable to equation 5 has been derived expressing D/D_0 as a function of the axial ratio of plate-like ellipsoids. (3) The various particles might have partial specific volumes in solution greater than those used in computing the equivalent spheres, that is, the particles in solution may actually be hydrated. In the computation of the b/a values presented in figure 8, it was assumed that the protein particles are rod-like ellipsoids of revolution and equation 5 was used for the evaluations.

tion having the higher intrinsic viscosity showed a double boundary in the ultracentrifuge and a bimodal distribution of particle lengths in the electron micrograph (45), both results indicating the first stage of end-to-end aggregation of a fraction of the particles. Its viscosity is about the same as that reported for different preparations by the author (44) and by Frampton and Neurath (25). As was pointed out by the author (44) and demonstrated by Robinson (63), the viscosity of tobacco mosaic virus measured in a capillary viscometer should be somewhat too low, owing to the partial orientation of the particles in the flowing stream. This effect was particularly pronounced in the case of the very highly aggregated virus material studied by Robinson. It should certainly be of a much lower magnitude in the cases of the unaggregated material and the very slightly aggregated material employed in the present instance.

The justification of the assumption that hydration is not the most important factor contributing to the inequality of D and D_0 is not difficult. For most of the data represented in figure 8, it would be necessary to assume that the particles swell to from three to forty times their dry volumes in order to explain the observed D/D_0 values solely in terms of hydration. Such an assumption seems absurd. Furthermore, when the supposed hydrodynamic volumes obtained from D/D_0 ratios are plotted against the measured viscosities, a line with a slope about fifty per cent greater than the 2.50 required by the Einstein equation (equation 1) for spheres is obtained. Since, as will be demonstrated later, the Einstein relationship is quantitatively correct for large spheres, this is strong evidence against the belief that hydration plays the dominant rôle in determining the D/D_0 ratios of proteins. However, it may account for a small portion of the effect.

It is not certain that the choice of the rod shape over the plate shape as the model for all protein particles is entirely justifiable, for it is not possible to decide with assurance, on the basis of an empirical consideration of sedimentation, diffusion, and viscosity data, whether protein particles are rod-shaped or plate-shaped. Some may have one shape and some the other. There is, however, excellent independent evidence that at least a few of the proteins represented in figure 8 are rod-like rather than plate-like. Oncley (57) and Ferry and Oncley (18) have shown that the dielectric dispersion curves of serum albumin and serum pseudoglobulin depart markedly from the Debye prediction for spheres. They were able to demonstrate, moreover, that the experimental curves can be anticipated theoretically if the two proteins are regarded as being rod-shaped ellipsoids with dipole angles of 45°. It was not found possible to predict these curves on the assumption of plate-like shapes. In the case of tobacco mosaic virus protein, a great deal of evidence has been amassed to show that the component particles are rod-shaped (46, 47). Recently obtained electron micrographs demonstrate the correctness of this conclusion, as is illustrated in figure 9 (72). Finally, as will be shown later, if the theoretical viscosity equations of Simha are regarded as being essentially valid, it is possible to conclude that viscosity, sedimentation, and diffusion data favor the interpretation that most of the proteins thus far investigated are rods rather than plates. Nevertheless, it is necessary to consider the possibility that some proteins are plate-like in shape. Whatever their shapes may be, it seems possible to conclude cautiously and tentatively that there is a quantitative correlation between the axial ratios of protein particles and their intrinsic viscosities.

C. Rod-like models

Experiments on the intrinsic viscosity of rod-like models have been reported by Eirich, Margaretha, and Bunzl (15). Natural silk fibers with a diameter of 40μ were cut into several distinct lengths in order to produce relatively homogeneous batches of rod-like particles. The smallest had an axial ratio of 5:1, and the largest a ratio of 23:1. Portions of some of these preparations were agitated so as to split the fibers. Various homogeneous batches with axial

ratios between 32:1 and 140:1 were obtained in this manner.   Then artificial
silk strands with diameters of 9 μ were cut into various lengths to give particles
with axial ratios of 25:1, 50:1, 75:1, and 100:1.   Naturally, all of these dimen-
sions were checked by methods involving the use of the microscope.   The various
rod models were suspended in a mixed solvent of tetrachloroethane and olive
oil, and their viscosities were studied in Couette, Ostwald, and pressure vis-
cometers.   In figure 10 are shown the data obtained in a Couette viscometer.
Here specific viscosity is plotted against concentration for the various axial
ratio values.   It is evident that increasing axial ratios of such rod-like models
parallel increasing viscosities.   Here, then, there is a very definitely established
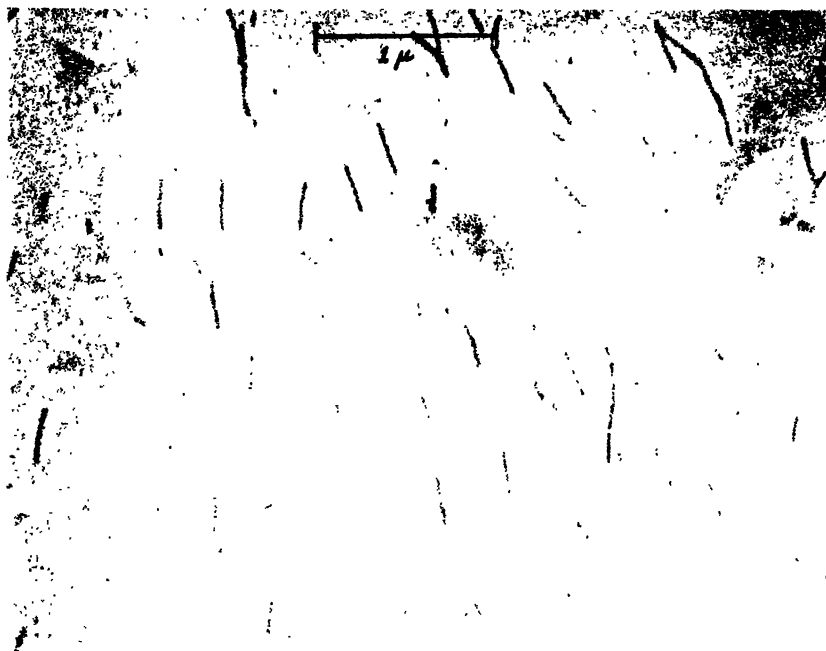
FIG. 9. Electron micrograph of tobacco mosaic virus particles × 24,000.   (From Stanley
and Anderson (72).)

correlation between viscosity and axial ratio.   There is no correlation between
intrinsic viscosity and particle weight, particle length, or particle diameter,
however.

When these data and those on proteins are considered together, it seems that
a good case can be established for the existence of a connection between the
intrinsic viscosity and the axial ratio of rigid particles.   In reality, this conclu-
sion is in complete harmony with the previously drawn conclusion that, within
homologous series of linear polymers or linear molecules, intrinsic viscosity de-
pends upon molecular weight.   In an homologous series, all of the particles are
probably of the same thickness.   Hence, molecular weights within a series are
proportional to axial ratios.   Therefore, all of the data considered thus far point

to the conclusion that the intrinsic viscosity of a suspension or solution of anisometric particles is a function of the ratio of length to thickness of the particles.

III. AN EXPERIMENTAL EXAMINATION OF THE HYDRODYNAMIC APPROACH

Many attempts have been made in recent years to account theoretically for the relationship just observed between the intrinsic viscosity and the shape of
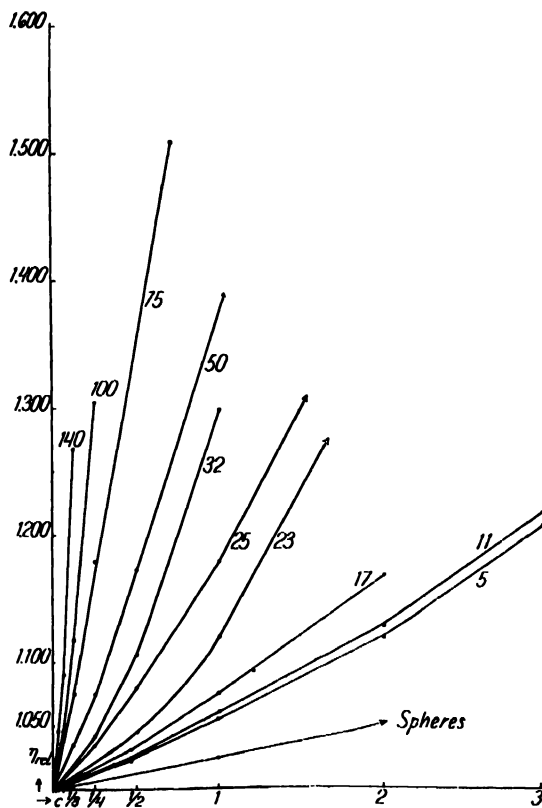
FIG. 10. Relative viscosities of various suspensions of rod-like models plotted as a function of volume per cent concentration. Numbers indicate the ratios of length to thickness of the particular particles for which each curve was obtained. (From Eirich, Margaretha, and Bunzl (15).)

particles in suspension or solution. Most of these approaches have been based upon hydrodynamic considerations. Stated crudely, the hydrodynamic viewpoint is that, in a pure liquid undergoing plane laminar flow, infinitesimal layers of the liquid glide over one another, each layer moving with a velocity slightly less than that of its neighbor on one side and slightly greater than that of its neighbor on the other side. In this process energy is dissipated, accounting for the viscosity of the liquid. If a rigid solid object, large compared to the infini-

tesimal layers of liquid, i.e., large compared to the dimensions of the fluid particles, is placed in such a flowing system, some layers of the liquid will move faster than the particle and some slower.   Hence, liquid will have to flow around the obstruction.   This disturbance in the motion of the fluid results in an added dissipation of energy by the system, that is, in increased viscosity.

A. The viscosity of spherical particles

The simplest application of the hydrodynamic approach to this general question was made by Einstein (12) in deriving equation 1, which describes the viscosity of a suspension of rigid spheres, large with respect to the dimensions of
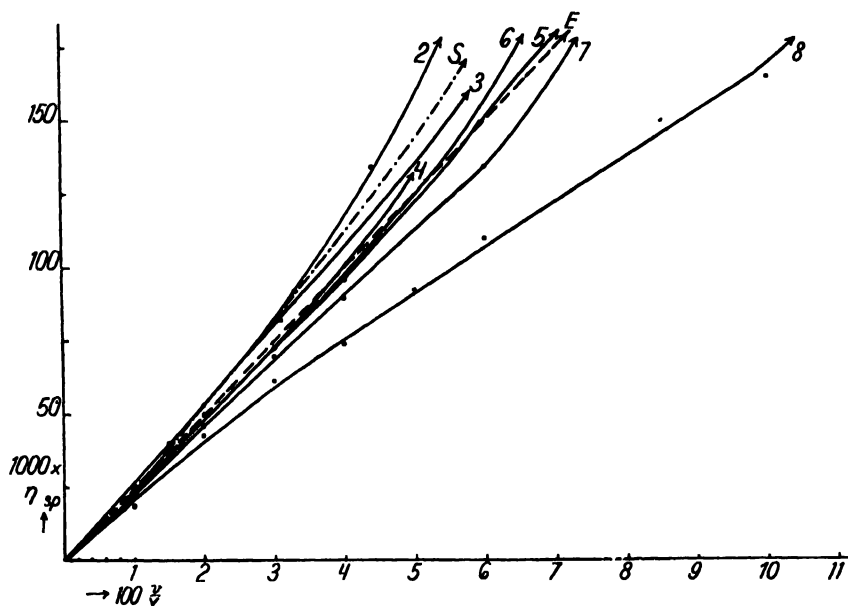
Fig. 11. Specific viscosities plotted against volume concentrations for glass spheres in mercuric nitrate-nitric acid (4, 5, 7, 8), mushroom spores in olive oil-tetrachloroethane (2, 3), and yeast in water (6).   Curve E is graph of Einstein equation (equation 1), and curve S is graph of Einstein equation with second-order term.   (From Eirich, Bunzl, and Margaretha (14).)

the particles of the fluid and small with respect to the dimensions of the viscometer.   If an explanation of the relatively complex viscosity behavior of rod-like or thread-like materials is to be sought on the basis of hydrodynamic theory, it is of the utmost importance that the validity of this simplest of applications of such theory be ascertained.   Eirich, Bunzl, and Margaretha (14) have considered the matter experimentally.   They studied the viscosity of glass spheres with a radius of 80 microns suspended in a mercuric nitrate–nitric acid solution, that of mushroom spores with a radius of 4 microns dispersed in an olive oil-tetrachloroethane mixture, and that of yeast with an average radius of 2.5 microns dispersed in water, using Couette, capillary, and falling-ball vis-

cometers.   The spherical natures of all of these particles were ascertained by microscopic examination.   In figure 11 specific viscosities are plotted against volume concentrations for the three suspensions.   It is evident that the limiting slopes of all of these viscosity–concentration curves approach that demanded by the Einstein equation, with a maximum deviation of less than 10 per cent. These results demonstrate quite conclusively the applicability of the Einstein equation to the situations for which it was derived.   In view of this, it seems justifiable to proceed to the more complex problem, namely, the examination of the application of hydrodynamic theory to the relationship between the viscosity and the shape of non-spherical particles.
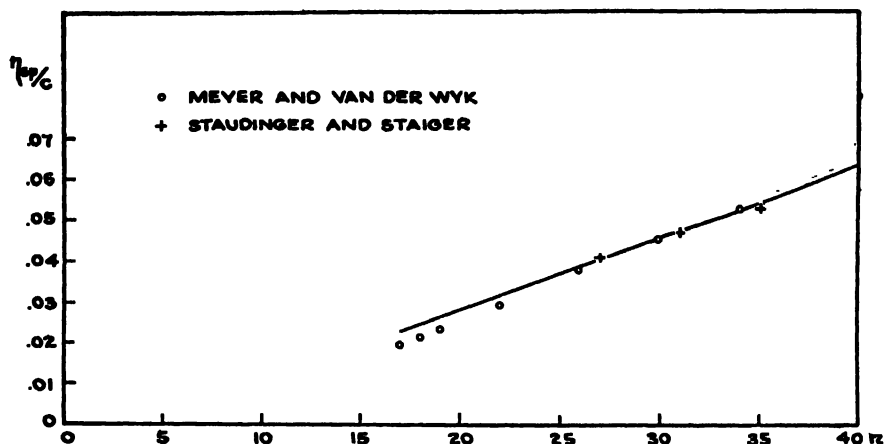
Fig. 12. Base molar intrinsic viscosity of normal hydrocarbons plotted against number of carbon atoms in chain.   Smooth curve is plot of Huggins' theoretical equation for randomly kinked chain.   Data were taken from Staudinger and Staiger (79) and from Meyer and van der Wyk (54).   (From Huggins (30).)

B. The viscosity of randomly kinked chains

Huggins (29, 30) has extended Kuhn's (42) hydrodynamic treatment of the case of a chain of spheres to consider the case of a randomly kinked chain of spheres.   Such a system ought to represent a fair model of most of the natural and synthetic linear polymers and compounds considered earlier in this review. An expression which can be reduced to the form of equation 2, that is, to a form which expresses intrinsic viscosity as a linear function of the molecular weight or of the number of repeat units, was obtained.   Figure 12, taken from one of Huggins' publications (30), shows how his equation may be made to fit the data of Meyer and van der Wyk and of Staudinger and Staiger discussed earlier. Agreement of this sort can be regarded as being most encouraging.   Because it was assumed that the interaction between the individual spheres of the kinked chains and the surrounding medium was that of very small spheres, Huggins' treatment is able to account for intrinsic viscosities less than 2.5.   Alfrey, Bartovics, and Mark (1) have been able to account for the effect of temperature

and solvent type on the intrinsic viscosity of polymer solutions on the basis of theoretical considerations similar to those of Huggins.

C. *The viscosity of rigid ellipsoids*

It is yet necessary to discuss only the various attempts that have been made to relate the intrinsic viscosity of rigid ellipsoids to axial ratios. These treatments are continuations and modifications of Jeffrey's (31) original extension of the Einstein development for large spheres. In considering the intrinsic viscosity of anisometric particles, three distinct cases must be recognized: (*1*) the case in which the particles are under the influence of complete Brownian movement; (*2*) the case in which there is no Brownian movement; (*3*) the intermediate
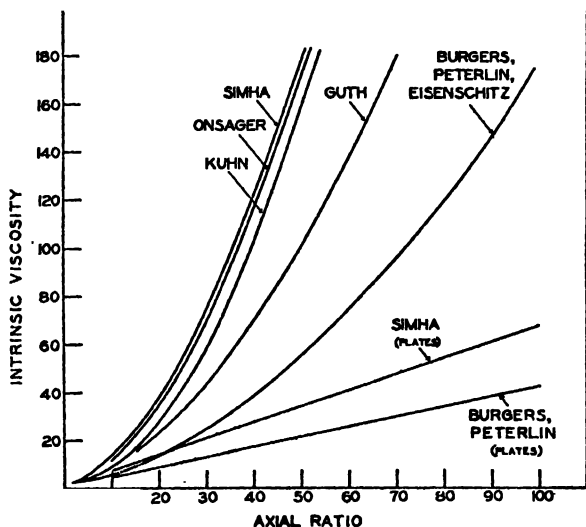
FIG. 13. Graphs of various theoretical equations expressing relationships between the volume fraction intrinsic viscosities of colloidal solutions with complete Brownian motion and the axial ratios of rod-like (undesignated graphs) and plate-like ellipsoids of revolution considered as models of the colloidal particles.

case. A great many equations have been derived relating axial ratios to the intrinsic viscosity of both rod-like and plate-like ellipsoids under the influence of complete Brownian motion (6, 7, 17, 27, 42, 59, 61, 69). These are summarized graphically in figure 13. The various equations predict that the intrinsic viscosities of rod-like ellipsoids will be greater than that of spheres by amounts which are roughly functions of the squares of the axial ratios. The Simha (69) equation predicts a much higher viscosity than the others. This is due to the fact that the effect of Brownian motion is considered more rigorously in this derivation than in the others. Compared to that of rods, the viscosity of plate-like ellipsoids is relatively insensitive to changes in the axial ratio.

The smooth curve fitting the data in figure 9 is Simha's theoretical curve for rod-like particles. The agreement between the theoretical relationship of par-

ticle shape to intrinsic viscosity and the data obtained with proteins is indeed very satisfactory. Using some of these same data, Mehl, Oncley, and Simha (52) computed the axial ratios from diffusion and sedimentation measurements, first, on the assumption that the particles are rod-shaped and, second, on the assumption that they are plate-shaped. Then, using Simha's equation for rods and for plates, they calculated the axial ratios from viscosity data for both cases. It can be observed in table 2, which summarizes their results, that the agreement between the values calculated from diffusion and sedimentation on the one hand and from viscosity on the other hand is very excellent when it is assumed that the particles are rods and just fair when it is assumed that they are plates. As was mentioned previously, this may be taken as a rather feeble indication that most of the proteins are indeed rods.

TABLE 2

The shapes of protein molecules (52)

PROTEIN	D_0/D	η_{sp}/G	b/a, ELONGATED		a/b, FLATTENED	
			Diffusion	Viscosity	Diffusion	Viscosity
Egg albumin..................	1.17	5.7	3.8	5.0	4.0	6.7
Serum albumin...............	1.25	6.5	5.0	5.6	5.4	7.7
Hemoglobin...................	1.16	5.3	3.7	4.6	3.9	6.0
Amandin.....................	1.28	7.0	5.4	6.0	6.0	8.5
Octopus hemocyanin..........	1.38	9.0	7.2	7.3	8.2	11.4
Gliadin......................	1.60	14.6	10.9	10.5	13.6	21
Homarus hemocyanin.........	1.27	6.4	5.2	5.5	5.8	7.5
Helix pomatia hemocyanin.....	1.24	6.4	4.8	5.5	5.2	7.5
Serum globulin...............	1.41	9.0	7.6	7.3	8.9	11.4
Thyroglobulin................	1.43	9.9	7.8	7.9	9.2	12.7
Lactoglobulin................	1.26	6.0	5.2	5.1	5.7	6.9
Pepsin.......................	1.08	5.2	2.5	4.5	2.6	5.8
Helix hemocyanin (pH 8.6)....	1.89	18.0	16.6	12.0	23.9	26

Because of the large size of the particles involved, the data of Eirich and collaborators (15) on visible rod-like models exemplify the condition in which there is no Brownian motion. In figure 14 the intrinsic viscosities of Eirich's various rod-like model suspensions are plotted against the axial ratios of the fractions. The two lower curves are the results of the two theoretical treatments of this case (16, 31). Although there is qualitative agreement, as yet no satisfactory quantitative agreement between theoretical and observed relationships of intrinsic viscosity to axial ratios has been attained for the case of rod-like particles not under the influence of thermal movement.

Solutions of tobacco mosaic virus, especially those of highly aggregated preparations, are representative of systems with intermediate Brownian motion. The virus particles in solution do not have dominant or complete Brownian motion, because the solutions exhibit double refraction of flow,—a condition due to the partial or complete orientation of the rod-like particles by the flowing stream (46). However, Brownian movement is not completely overshadowed

by the orienting tendency of the flowing field in the case of virus particles, because the intensity of double refraction of flow is a function of the flow-velocity gradient, and because the average orientation of the particles as measured by the angle of isocline, a physical consideration related to the double refraction of flow, increases with increasing velocity gradients (51, 63). For intermediate systems such as this, it is possible to make three definite predictions from hydrodynamic theory in its present state of development: (1) The viscosity of even infinitely dilute systems of this sort should be anomalous,—that is, the viscosity coefficient measured in very low velocity gradients should be greater than that measured in higher gradients. This follows simply from the hydrodynamic consideration that rods randomly oriented contribute more to the viscosity of a system than rods oriented parallel to the direction of flow.
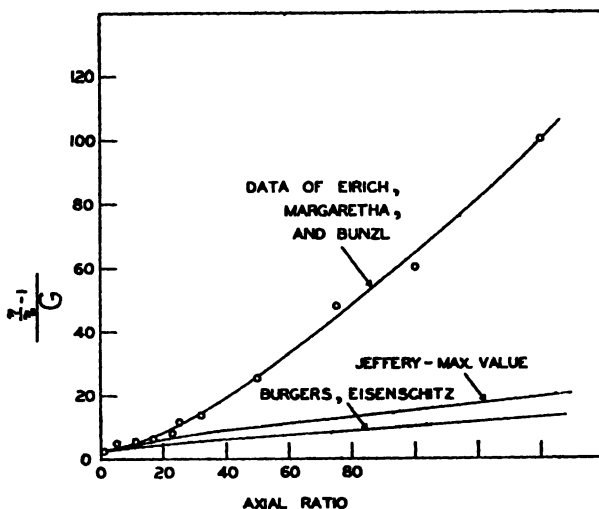
Fig. 14. Volume fraction intrinsic viscosities of suspensions of rod-like models plotted against axial ratios. Upper curve, data of Eirich, Margaretha, and Bunzl (15); lower two curves, graphs of theoretical equations derived for particles with no Brownian motion (16, 31).

(2) The decrease in the viscosity coefficient as the velocity gradient is increased should be paralleled by an increase in the intensity of double refraction of flow and by an increase in the average orientation of particles as determined by measurements of the angle of isocline. (3) For intermediate velocity gradients, a *positive* temperature coefficient of relative or of intrinsic viscosity should be obtained, but at very high and at very low gradients the temperature coefficient should approach zero. This follows simply from the fact that in intermediate gradients where the rods are partially oriented, increasing the temperature increases the randomness of the particles, thereby increasing their contribution to viscosity. In very high gradients, where Brownian motion is completely dominated, or in very low gradients where it is completely dominant, no such effect can ensue.

Robinson (63) has studied exceedingly dilute tobacco mosaic virus solutions in a Couette-type viscometer equipped with an optical system for measuring double refraction of flow and the angle of isocline.   Figure 15 is a diagram showing the relative viscosity of a 0.02 per cent tobacco mosaic virus solution plotted
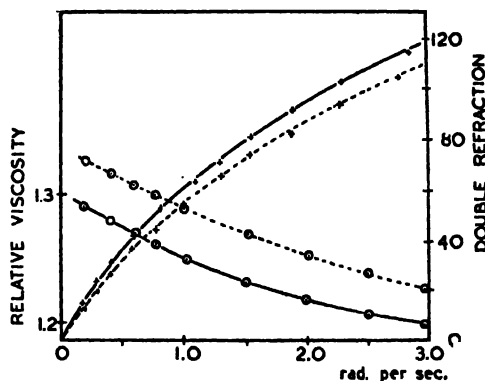
FIG. 15. Relative viscosity (o) and intensity of double refraction of flow (+) of 0.02 per cent tobacco mosaic virus solution plotted against angular velocity of rotating cylinder of viscometer. ———, at 14.4°C.; - - - -, at 19.6°C.   (From Robinson (63).)
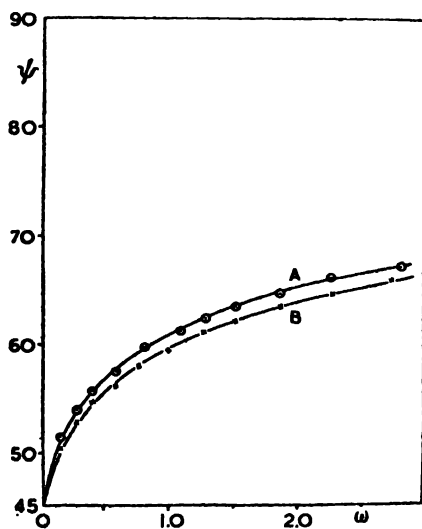
FIG. 16. Angle of isocline (ψ) of 0.02 per cent tobacco mosaic virus solution plotted against angular velocity (ω) of rotating cylinder.   Curve A at 14.4°C.; curve B at 19.6°C. (From Robinson (63).)

against the angular velocity of the rotating cylinder.   Exactly in accordance with the first prediction, the relative viscosity decreases as the velocity gradient increases.   Intensity of double refraction of flow is also plotted against velocity of flow in this figure, and in figure 16 the angle of isocline is plotted against

velocity of flow.   Exactly in accordance with the second prediction, the decrease
of relative viscosity with increase of velocity gradient is paralleled by an in-
crease in the intensity of double refraction and by an increase in the angle of
isocline.   It may also be observed in figure 15 that the relative viscosity of
tobacco mosaic virus is higher at 19.6°C..than at 14.4°C.   This is exactly in
accordance with the third prediction.   From an examination of figure 17, it is
evident that the positive temperature coefficient of the relative viscosity has a
maximum value for moderate velocity gradients, also exactly as predicted from
pure hydrodynamic considerations.   None of the currently discussed theories
of viscosity based on interaction concepts would predict a temperature relation-
ship such as this.   Furthermore, the relative viscosities of substances, such as
relatively concentrated gelatin solutions, for which one can reasonably ascribe
the viscosity to structure, have negative temperature coefficients.   In view of
this, it would seem that these experiments constitute perhaps the best confirma-
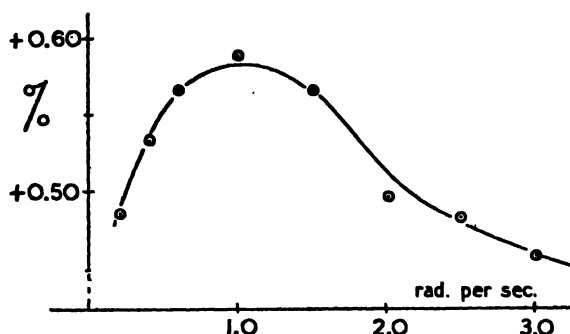
FIG. 17. Temperature coefficient of relative viscosity (ordinate) of 0.02 per cent tobacco
mosaic virus solution plotted against angular velocity.   (From Robinson (63).)

tion available at present of the validity of the hydrodynamic approach to the
description of the viscosity behavior of suspensions of rigid ellipsoids.

D. General conclusions

The experimental data which have been examined in connection with the
hydrodynamic approach have brought out several facts: (1) The equation de-
rived by the hydrodynamic method for the viscosity of spheres in suspension
was found to be entirely in accord with the results of experiments designed to
test it critically.   (2) The hydrodynamic method can be used to obtain an
equation predicting a linear relationship between the intrinsic viscosity and the
molecular weight of chain molecules and polymers.   Without making any un-
reasonable assumptions, this equation can be fitted to actual data with reason-
able success.   (3) The results of the hydrodynamic treatment for the case of
rigid ellipsoids undergoing complete Brownian movement can be used to ration-
alize quantitatively the experimental data obtained on proteins by viscosity
methods, on the one hand, and diffusion and sedimentation methods, on the
other hand.   (4) Results of hydrodynamic consideration are in qualitative,

though not quantitative, accord with viscosity data on rod-like models too large to have Brownian motion.   (5) Finally, hydrodynamic theory leads in a seemingly unique way to an explanation of the positive temperature coefficient of relative viscosity observed in solutions of rods with intermediate Brownian motion.   Whether or not these encouraging findings justify the acceptance as strictly valid of the equations thus far obtained by the hydrodynamic approach, they certainly justify further consideration of this type of theory in the search for an explanation of the connection between the intrinsic viscosity and the shape of suspended or dissolved particles.

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THE HALIDES AND OXYHALIDES OF SILICON[1, 2]

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The preparation and some of the properties of the silicon halides, oxyhalides, and related compounds are briefly described, with special reference to the results of recent research in this field. A comparison is offered of the compounds of silicon with those of carbon and of the elements in Group IV a; similarities and differences are pointed out. The possible application of the oxyhalides of silicon to the synthesis of silicon resins is suggested.

Recent interest in the preparation of silicon resins, the commercial possibilities of which have attracted the attention of a number of industrial research laboratories, suggests a consideration of recent developments in the study of the silicon halides and oxyhalides, from which such products may be derived. The halides and related compounds, such as the oxyhalides, the halohydrides, and the alkyl and aryl silicon halides, present a number of points of theoretical as well as practical importance. Especially worthy of emphasis are the differences in properties exhibited by silicon in these compounds in comparison with those of its analog, carbon, in spite of the strong resemblances in formula shown by the corresponding compounds of the two elements.

Table 1, while not complete, is intended to summarize the relative power of carbon, silicon, titanium, zirconium (and hafnium), and thorium to combine with the halogens. The similarities in the formulas of the compounds of silicon and carbon are clearly to be seen, as well as the differences between these two elements and the other elements constituting Group IVa of the Periodic Table. Sharp contrasts are to be noted, as follows: (*a*) the absence of chain compounds of titanium, zirconium, or thorium; (*b*) instead, the existence in the case of titanium and zirconium of halides in the trivalent and bivalent states; (*c*) the absence of haloforms, $MeHX_3$, and other halohydrides of all the elements other than carbon and silicon. For convenience recent work upon the silicon halides and related compounds will be discussed for the most part in the order of their arrangement in table 1.

I. FLUORIDES

Aside from the well-known tetrafluoride, SiF_4, discovered in 1771 by Scheele, the only other silicon fluoride that has been established definitely is the second member of the homologous series Si_nF_{2n+2}, that is, Si_2F_6, which was prepared by

E. L. Gamble and the writer in 1932 by the fluorination of Si_2Cl_6 with zinc fluoride (10). At low temperatures it is a colorless solid which sublimes at atmospheric pressure, its vapor pressure becoming 760 mm. at $-19.1°C$; its melting point is $-18.5°C$. at 780 mm. It is very rapidly hydrolyzed to form "silicoöxalic acid" (or 1,2-bis(oxyoxo)disilane), silicic acid, and fluosilicic acid.

TABLE 1

Halogen compounds of the elements of Group IVa

HALIDES	Carbon	Silicon	Titanium	Zirconium (Hafnium)	Thorium
Fluorides	CF_4 C_2F_6 C_2F_4 CHF_3 CH_2F_2 CH_3F	SiF_4 Si_2F_6 $SiHF_3$	TiF_4 TiF_3	ZrF_4 ZrF_3	ThF_4
Chlorides	CCl_4 C_2Cl_6 C_2Cl_4 C_6Cl_6 $CHCl_3$ CH_2Cl_2 CH_3Cl	$SiCl_4$ Si_2Cl_6 $(SiCl_2)_x$ $(SiCl)_x$ $SiHCl_3$ SiH_2Cl_2 SiH_3Cl	$TiCl_4$ $TiCl_3$ $TiCl_2$	$ZrCl_4$ $ZrCl_3$ $ZrCl_2$	$ThCl_4$
Bromides	CBr_4 C_2Br_6 C_2Br_4 C_6Br_6 $CHBr_3$ CH_2Br_2 CH_3Br	$SiBr_4$ Si_2Br_6 $SiHBr_3$ SiH_2Br_2 SiH_3Br	$TiBr_4$ $TiBr_3$ $TiBr_2$	$ZrBr_4$ $ZrBr_3$ $ZrBr_2$	$ThBr_4$
Iodides	CI_4 C_2I_4 C_6I_6 CHI_3 CH_2I_2 CH_3I	SiI_4 Si_2I_6 Si_2I_4 $SiHI_3$ SiH_2I_2 SiH_3I	TiI_4 TiI_3	ZrI_4 ZrI_2	ThI_4

The instability of the Si—Si bond is responsible for failure to prepare higher members of the series, such as Si_3F_8, from the corresponding chlorides.

The direct fluorination of silicon or of its alloys is a very vigorous reaction, the temperature at the zone of contact rising to incandescence; hence it is not surprising to find in this case that only the tetrafluoride can be obtained, the Si—Si linkages existing in the crystalline element being broken during the reaction.

So-called *subfluorides* of silicon, of unknown composition, have been reported by several investigators, including St. C. Deville (19) and Troost and Hautefeuille (20), who employed various methods intended to reduce the tetrafluoride. However, attempts by Ruff (7) to repeat this work were unsuccessful, nor could he obtain evidence of a subfluoride by means other than those previously tried. The evidence for the existence of such lower fluorides therefore must be considered as questionable. Similarly, up to the present the existence of silicon oxyfluorides has not been established.[3]

The absence of subfluorides of silicon is directly associated with the fact that silicon, like carbon and—somewhat unexpectedly—like thorium, but unlike the other elements in the fourth periodic group, is uniformly quadrivalent in its halogen compounds. Although lower halides, such as $(SiCl_2)_x$ and even $(SiCl)_x$, have been formed by reduction of silicon tetrachloride with hydrogen under proper conditions, these unsaturated polymerized substances are not to be regarded as lower valence compounds of silicon.

Mention of the case of hydrolysis of hexafluorodisilane, Si_2F_6, leads to the observation that the fluorine compounds of silicon deviate in several particulars from the otherwise constant behavior of the halides toward water, i.e., a vigorous and usually complete replacement of halogen by hydroxyl with accompanying condensation to produce siloxane linkages, Si—O—Si. In the case of silicon tetrafluoride, however, owing to the comparatively small atomic radius of the fluorine atom, a coördination number of six for the silicon atom is assumed in the formation of soluble fluosilicic acid, in addition to insoluble hydrous silica. Various mechanisms for this reaction have been suggested, but a plausible interpretation appears to be that the complete replacement of the fluorine atoms by hydroxyl and the consequent formation of hydrous silica and hydrofluoric acid is at once followed by interaction of these products, with solution of the silica to a greater or less extent, forming fluosilicic acid. Toward the halogen atoms of larger atomic radius silicon does not show a coördination number greater than four.

Another instance of exceptional behavior on the part of the fluorides of silicon is found in the case of the triphenylhalosilanes, $(C_6H_5)_3SiX$. The case of hydrolysis of these substances decreases from iodide to fluoride, as the strength of the Si—X bond increases, so that $(C_6H_5)_3SiF$ is said to be unaffected by water (6), whereas the corresponding chloro and bromo compounds are rapidly hydrolyzed, forming silicols.

II. CHLORIDES

The interaction of elementary silicon, or better, of a silicon alloy, with chlorine differs from the direct fluorination of silicon in that notable quantities of the higher chlorides of the series Si_nCl_{2n+2} may be obtained, especially if the

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[3] Since the presentation of this review, H. S. Booth and R. A. Osten at a meeting of the American Chemical Society held in Buffalo, New York, September 8, 1942, have reported the successful preparation of an oxyfluoride, Si_2OF_6, from Si_2OCl_6 by means of antimony trifluoride, together with several intermediate fluorochloro derivatives of disiloxane.

temperature employed is held as low as practicable. At high temperatures the tetrachloride is almost exclusively formed, a fact which led Martin (5) to conclude that the initial compounds produced on chlorination of silicon are the most complex, with chains of Si—Si linkages, such as were present in the element itself; in the presence of excess chlorine, and aided by higher temperatures, these linkages are progressively broken down, yielding finally the tetrachloride.
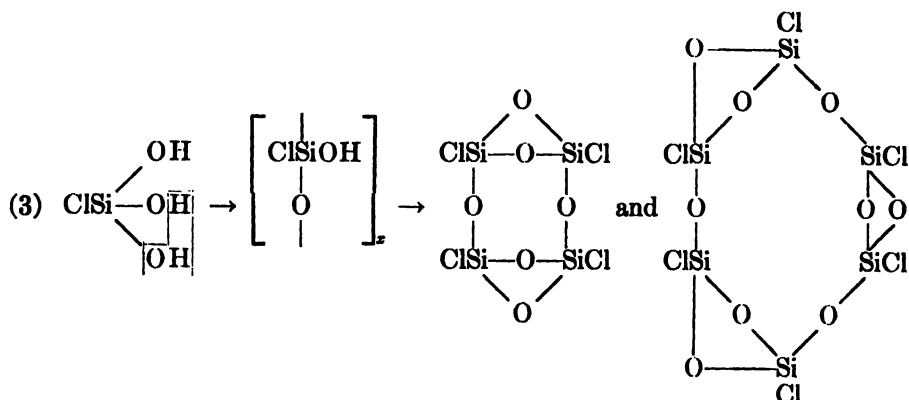
For the preparation of these higher chlorides we have found (12) that commercial "calcium silicon," containing 60–65 per cent silicon and 35–30 per cent calcium, gives the best results. From the crude reaction product yields of hexachlorodisilane, Si_2Cl_6, up to 25 per cent were obtainable, rapidly diminishing proportions of Si_3Cl_8 and higher halides also being formed.

It is perhaps of interest to note that, instead of elementary chlorine, certain anhydrous metal chlorides, such as cuprous or cupric chlorides or lead chloride, may be used; in some instances the tetrachloride is obtained in a practically pure condition on heating the mixture of metal chloride and silicon. This displacement reaction is of rather general application; thus we have prepared samples of silicon tetraiodide from heated mixtures of cuprous iodide or of red mercuric iodide and silicon, some purification of the product here being found necessary. Likewise, the reaction between cuprous bromide and silicon yields silicon tetrabromide, and the tetrafluoride results from heating a mixture of silicon powder and lead fluoride.

As to the unsaturated silicon chlorides, only the polymerized dichloride, $(SiCl_2)_x$, and the monochloride, $(SiCl)_x$, are reported to have been prepared (15, 16), the former by reduction of the tetrachloride with hydrogen in a glow discharge from aluminum electrodes, the latter by the "cracking" of $Si_{10}Cl_{22}$ (or of $Si_{10}Cl_{20}H_2$) in an inert atmosphere. The "dichloride" is described as a white stable solid, which is soluble in methyl alcohol and is decomposed violently by water with evolution of hydrogen. The "monochloride," $(SiCl)_x$, is said to be a yellow amorphous solid, changing reversibly to orange red between 180° and 200°C., and to be inflammable in air at 100°C. No report has appeared as yet in confirmation of this work; however, from similar but unsuccessful attempts to prepare the corresponding bromides, we conclude that the yields of the unsaturated halides obtainable by this process must be very meagre.

In connection with Schwarz' work, it is interesting to observe that the remarkable compounds, $Si_{10}Cl_{22}$ (17) and $Si_{10}Cl_{20}H_2$ (18), obtained by him by the reaction of the tetrachloride and its decomposition products with hydrogen in a so-called "hot-cold" tube, represent the longest straight-chain compounds of silicon known, with a formula weight in the case of $Si_{10}Cl_{22}$ of 1060. Oddly enough, intermediate chlorides which might have been expected to form, such as Si_6Cl_{14} to Si_9Cl_{20}, inclusive, were not observed in the reaction product.

From what we know of the hydrolysis of halides of other elements, it might be inferred that the interaction of water with the tetrahalides of silicon should proceed stepwise, with the formation of such intermediate compounds as $SiCl_3OH$, $SiCl_2(OH)_2$, and $SiCl(OH)_3$, which on condensation would yield oxychlorides containing siloxane linkages. Thus:

(1) Cl_3Si—[OH   H]—$OSiCl_3$ → Cl_3Si—O—$SiCl_3$ or Si_2OCl_6

(2)

$$
\begin{array}{ccc}
Cl_2SiO\text{—[}H \quad HO\text{]—}SiCl_2 \\
| \qquad\qquad\qquad | \\
[HO] \qquad\qquad [OH] \\
| \qquad\qquad\qquad | \\
[H]O \qquad\qquad O[H] \\
| \qquad\qquad\qquad | \\
Cl_2Si\text{—O—[}H \quad HO\text{]—}SiCl_2
\end{array}
\rightarrow
\begin{array}{c}
Cl_2Si\text{—O—}SiCl_2 \\
| \qquad\qquad | \\
O \qquad\quad O \\
| \qquad\qquad | \\
Cl_2Si\text{—O—}SiCl_2
\end{array}
\text{ or } (SiOCl_2)_4
$$

(3)

$$
\begin{array}{c}
\quad OH \\
\quad / \\
ClSi\text{—O[}H] \\
\quad \backslash \\
\quad [OH]
\end{array}
\rightarrow
\left[
\begin{array}{c}
| \\
ClSiOH \\
| \\
O \\
|
\end{array}
\right]_x
\rightarrow
\begin{array}{c}
\quad O \\
\; / \quad \backslash \\
ClSi\text{—O—}SiCl \\
| \qquad\qquad | \\
O \qquad\qquad O \\
| \qquad\qquad | \\
ClSi\text{—O—}SiCl \\
\; \backslash \quad / \\
\quad O
\end{array}
\text{ and }
\begin{array}{c}
\qquad\qquad Cl \\
O\text{———}Si \\
\; / \quad\quad O \quad O \\
ClSi \qquad\qquad SiCl \\
| \qquad\qquad\quad O\;O \\
O \qquad\qquad\quad \backslash / \\
ClSi \qquad\qquad SiCl \\
\; \backslash \quad O \quad O \\
O\text{———}Si \\
\qquad\qquad Cl
\end{array}
$$
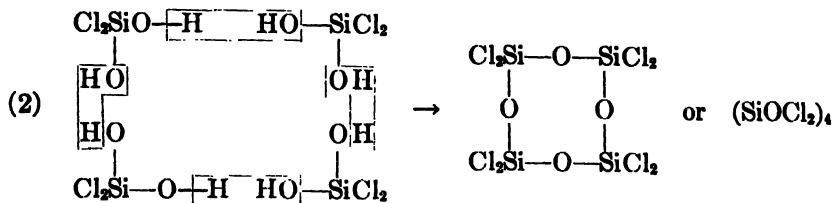
The first two of these oxychlorides are well-established compounds; the third corresponds to a compound of unknown molecular weight, $(Si_2O_3Cl_2)_x$, reported by Troost and Hautefeuille (21), the existence of which, however, is not supported by adequate experimental data. In its simplest forms it would be represented by a dimeric structure containing three oxygen atoms bridged between two silicon atoms, as in

$$
\begin{array}{c}
\qquad O \\
\; / \quad \backslash \\
Cl\text{—}Si\text{—O—}Si\text{—}Cl \\
\; \backslash \quad / \\
\qquad O
\end{array}
$$
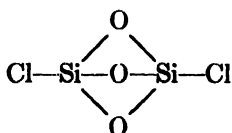
This substance, as well as the dimeric and trimeric forms of $SiOCl_2$, have not been isolated. Furthermore, none of the structures represented under (3) are probable, inasmuch as the bridging of two or three oxygen atoms between two silicon atoms violates the structural requirements known to hold among silicates.

Except under special conditions provided to retard the progress of hydrolysis, such intermediate compounds, if formed, are not isolated. In recent experiments, not yet completed, we have established the fact that, by diluting the silicon halide with anhydrous ether (or other organic solvents) and using a moist organic solvent, such as moist ether, as the hydrolytic medium, the hydrolysis of silicon tetrachloride may be controlled so as to form appreciable quantities of oxychlorides. The success of these experiments upon the partial hydrolysis of the tetrachloride suggests that even in the case of the tetrafluoride

the restraining influence of dilution of the reacting substances by inert solvents might conceivably lead to the isolation of the oxyfluorides of silicon.

III. BROMIDES

As with the chlorides of silicon, an homologous series of bromides, Si_nBr_{2n+2}, is known, the first member of which, the tetrabromide, is a liquid. The succeeding members of the series,—known definitely only as far as Si_4Br_{10},—are white crystalline solids. Their reactions, notably hydrolysis and ammonolysis, follow closely those of the corresponding chlorides.

A satisfactory method of preparation of hexabromodisilane, Si_2Br_6, was found accidentally by us a few years ago in an experiment intended to yield the oxybromides of silicon. With the aim of simultaneously oxidizing and brominating silicon, and in order to operate at as low a reaction temperature as possible, a mixture of oxygen and bromine vapor was passed over calcium silicide at 180–200°C. The product obtained consisted almost entirely of hexabromodisilane with but minute amounts of oxybromides, whereas, when elementary crystalline silicon was subjected to similar treatment, the main product formed was a mixture of the oxybromides. Evidently the energetic combination of the calcium in the silicide with oxygen facilitates the union of the silicon atoms—probably covalently linked together in $CaSi_2$—with bromine at a sufficiently low temperature to avoid splitting the Si—Si linkages.

IV. IODIDES

Less work has been done with the iodides of silicon than with the other halides of this element, in part, perhaps, because of the unstable character of these compounds on exposure to air and to light. Thus the tetraiodide, a white crystalline solid, which is obtainable, for example, when the vapors of iodine, entrained in a current of carbon dioxide, are passed over hot silicon, turns dark when left in a sealed glass tube in direct sunlight. Iodine also is liberated when the compound is left in contact with the air. Besides the tetraiodide, only the second member, hexaiododisilane, Si_2I_6, of the homologous series Si_nI_{2n+2} has been reported. It is a white crystalline solid, prepared by heating the tetraiodide with finely divided silver in a sealed tube at about 300°C.

The unsaturated compound Si_2I_4, tetraiododisilene, described as an orange-colored solid, is reported to result, together with the tetraiodide, from the thermal decomposition of hexaiododisilane. It represents the analog of the polymerized dichloride, $(SiCl_2)_x$.

V. HALOSILANES

In recent work on the iodo compounds of silane by Eméleus and coworkers (2), most of the gaps left in the list of known halosilanes have been filled. All of the possible compounds of the general formula SiH_nX_{4-n} had been recorded previously except the mono- and di-iodosilanes, SiH_3I and SiH_2I_2 (also styled "silyl" and "silylene" iodides), and the corresponding fluoro compounds. The iodo compounds have now been prepared by the reaction of silane with hydrogen

iodide at 80°C. under reduced pressure. Both substances are decomposed by light and have pungent odors. Monoiodosilane boils at 149.5°C. and melts at −1°C.; the diiodo compound boils at 45.4°C. and melts at −57°C.

In connection with the properties of these halosilanes it is perhaps worth recalling that some of them form explosive mixtures with ordinary air. We have experienced the explosion of a flask containing silicochloroform (trichlorosilane) while the apparatus was standing undisturbed at room temperature, the only explanation being the probable presence of air in the flask. Silicoiodoform similarly forms explosive mixtures with air. Silicobromoform when poured through the air burns brilliantly, liberating much smoke.

VI. MIXED HALIDES

In addition to the compounds listed in table 1 there may be mentioned the mixed halides formed by carbon and silicon (and to a less important degree by titanium), in which two or three different halogens are linked to carbon or silicon. Some of these compounds of silicon have long been known; others have been prepared only recently. Thus, while complete series of silicon chlorobromides, chloroiodides, and bromoiodides are recorded, the isolation of some of which dates back many decades, the fluorochlorides were first described in 1932 (1, 11), the fluorobromides in 1936 (8), and two fluorochlorobromides, $SiFClBr_2$ and $SiFCl_2Br$, in 1937 (9). As would be expected, these compounds exhibit properties resembling those of the binary halides from which they are derived.

The preparation of a silicon mixed halide with four different atoms attached to the silicon, as in $SiFClBrI$ or $SiHFClBr$, which would present the interesting possibility of optical isomerism, as yet has not been realized.

VII. OXYHALIDES

A few years ago a study of the various possible methods of preparation of the silicon oxybromides was carried out in our laboratory (14). In this study it was found that the reaction of a mixture of oxygen and the halogen with heated silicon, or the oxidation of the silicon tetrahalide, gave the most satisfactory results. By each of these methods a crude product was obtained which on careful fractionation proved to be a mixture of six or more oxybromides, all but one of which belonged to the homologous series $Si_nO_{n-1}Br_{2n+2}$. The exceptional case was the cyclic tetramer, $(SiOBr_2)_4$. Previous fragmentary work on the oxychlorides had not revealed the existence of such series, although they were to be expected. More recently we have established in another investigation (13) the fact that an entirely analogous series of oxychlorides exists, probably extending considerably beyond $Si_7O_6Cl_{16}$, which was the highest member isolated. All of these substances except the tetramer $(SiOCl_2)_4$— a colorless, crystalline solid—are colorless, oily liquids, which are hydrolyzed in the presence of moisture (the lower members most readily), and are miscible with carbon tetrachloride, chloroform, carbon disulfide, or silicon tetrachloride. They are converted by absolute ethyl alcohol into the corresponding ethyl esters, which are colorless, oily liquids with high boiling points and are hydrolyzed only very slowly,

even by water at 100°C.   The ester produced from Si_2OCl_6 and cyclohexanol was found to be a white crystalline solid, melting at 217.1–217.6°C. and soluble in the solvents previously mentioned and in ether and alcohol.   Further investigation of these substances is in progress with a view toward their possible utilization in the production of silicon resins, which appear up to the present to have been derived exclusively from the tetrahalides, such as silicon tetrachloride. Thus in the recent work of Hyde and De Long (3), dihalosilanes containing phenyl groups, prepared from silicon tetrachloride by means of the Grignard reaction, were hydrolyzed with aqueous hydrochloric acid and resinous products were obtained which, if the treatment were not too prolonged, remained soluble in organic solvents.   Hydrolysis products derived from alkyl-substituted dihalosilanes likewise gave resinous materials when air was passed through the heated liquids.

Interest in the production of such resinous substances containing silicon is naturally to be expected, since by the partial replacement of carbon atoms by silicon a product possessing superior properties in some respects may be anticipated, such as an increased stability at elevated temperatures.

The opening of this field of research, with its prospects of considerable industrial importance, illustrates once again the hazardous character of a prediction that any particular line of investigation has been exhaused of further possibilities of development.   Thus in a lecture a few years ago, Kipping (4), who, more than any other single investigator, has contributed to our knowledge of organosilicon chemistry, concluded his remarks with the statement that in his opinion no likelihood of further notable developments existed in this branch of silicon chemistry.   However, in the progress of science the certainties of today have a habit of becoming the uncertainties of tomorrow.   So it is not at all surprising to find now that investigations are actively being pursued in various laboratories with the object of uncovering the possibilities which lie in the field of silicon plastics.   It is perhaps a little premature to assert that great developments are at hand in this direction, since for large-scale industrial application the economics of the problem are as important as the basic chemical discoveries.   Nevertheless, enough has been learned to prove the truth of the contention that in this, as in other instances, while the door to further opportunity in research sometimes may appear closed, it is never locked.

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